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(54) **METHOD FOR PREPARING CARBON FIBER  
PRECURSOR**

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(57) **ABSTRACT**

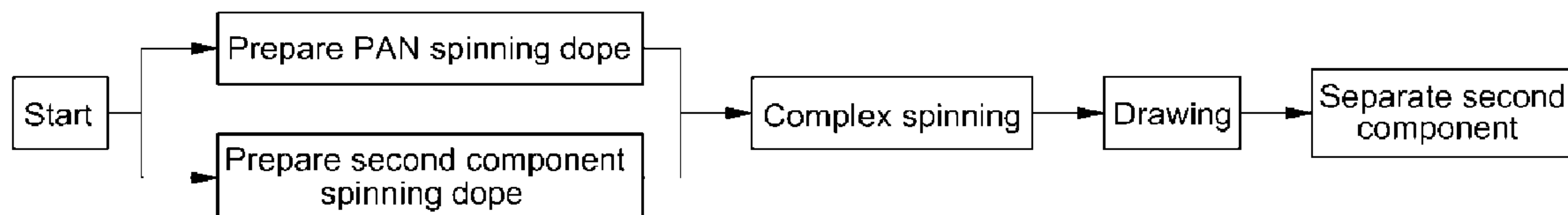
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Disclosed is a method for preparing a precursor fiber for a carbon fiber. The precursor fiber of fine denier according to the present invention is used to prepare a carbon fiber having excellent tensile strength and compressive strength by a conventional single component spinneret using a superdrawing process to prepare a high strength and high elastic carbon fiber with a reduction in stabilization time.



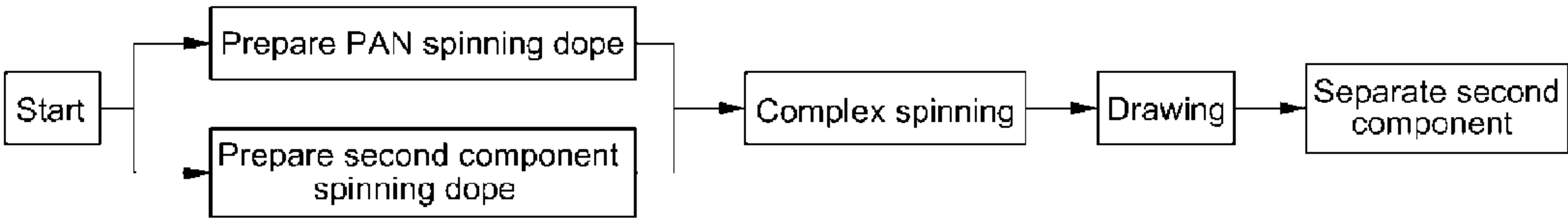


FIG.1

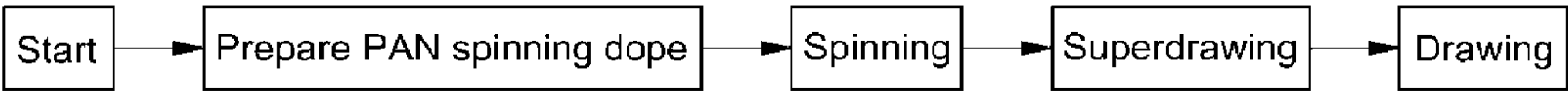


FIG.2



## METHOD FOR PREPARING CARBON FIBER PRECURSOR

### CROSS-REFERENCE TO RELATED APPLICATION

**[0001]** This application claims under 35 U.S.C. §119(a) the benefit of Korean Patent Application No. 10-2011-0122476 filed Nov. 22, 2011, the entire contents of which are incorporated herein by reference.

### BACKGROUND

**[0002]** (a) Technical Field

**[0003]** The present invention relates to a method for preparing a precursor fiber for a carbon fiber. More particularly, it relates to a method for preparing a precursor fiber of fine denier used to prepare a carbon fiber having excellent tensile strength and compressive strength by a conventional single component spinneret using a superdrawing process, thereby preparing a high strength and high elastic carbon fiber with a reduction in stabilization time.

**[0004]** (b) Background Art

**[0005]** Carbon fiber is a high strength (e.g., 3 to 7 GPa) and highly elastic (150 to 950 GPa) fiber containing more than 92% carbon and can be prepared by heat-treating a precursor material with a high carbon yield at a fairly high temperature. As the precursor material, an acrylonitrile polymer fiber having excellent tensile strength and compressive strength and high tensile modulus is most widely used. The degradation temperature of the acrylonitrile polymer is lower than the melting temperature, and thus it is difficult to perform melt-spinning. Some clothing fibers are mass-produced by melt-spinning using a plasticizer such as water. However, the acrylonitrile fiber for a carbon fiber is typically prepared by solution spinning. The acrylonitrile fiber prepared by solution spinning is drawn at a hydrothermal temperature (~100° C.) or subjected to multiple drawings to prepare a high performance carbon fiber (see the process diagram of FIG. 1). Typically, when an acrylonitrile undrawn yarn is drawn, the orientation of molecules occurs, and thus the degree of crystallization is increased.

**[0006]** Acrylonitrile drawn yarn as a precursor fiber is formed into a carbon fiber through a stabilization process (e.g., at 250 to 350° C.) in an oxidation atmosphere and a carbonization process (e.g., at 800 to 1,500° C.) in an inert atmosphere, and a graphitization process (e.g., at to below a temperature of 2,500° C.) is selectively performed. The stabilization process involves the cyclization of a Polyacrylonitrile (PAN) molecular structure and the combination of oxygen. For the combination of oxygen, the diffusion of oxygen into stabilized PAN fibers is required, and thus the stabilization time rapidly increases depending on the thickness of the fiber. During the carbonization process, ladder-like molecular structures formed in the stabilization process are bonded to each other and modified into graphite-like structures, and volatilization of elements other than carbon occurs. During the stabilization and carbonization processes, fiber contraction in the longitudinal direction occurs due to physical or chemical causes, which may reduce the molecular orientation of the finally obtained carbon fiber. Therefore, the carbon fiber may have a well-developed crystalline structure in the longitudinal direction by applying a tensile force to improve the molecular orientation during the stabilization and carbonization processes.

**[0007]** According to Griffith's flaw theory, if the same material is used, when the fiber diameter is reduced, the surface area per unit length is reduced, which reduces the probability of the occurrence of defects, thereby increasing the tensile strength. Therefore, when the diameter of the acrylonitrile precursor fiber is smaller, the tensile force per unit area can be increased during the stabilization and carbonization processes, thereby preparing a high strength carbon fiber. A spinneret with a relatively smaller hole is required to prepare a precursor fiber having a small diameter and, in particular, an expensive multi-component spinning machine, which can separate a desired fiber through a physical process (e.g., side-by-side fiber) or a chemical process (e.g., a islands-in-a-sea fiber) by simultaneously spinning at least two polymers, is required to prepare a superfine fiber.

**[0008]** International Patent Publication No. WO2009/049174 discloses a method for preparing an ultrafine carbon fiber having a high tensile strength of about 4.5 GPa through composite spinning in the form of core-shell (or sheath-core) or islands-in-a-sea. This method, however, has problems in that a process of melting or incinerating auxiliary components after the spinning as well as an expensive composite spinning machine significantly increases the manufacturing costs.

**[0009]** Moreover, U.S. Pat. No. 6,428,891 discloses a method for preparing a carbon fiber by wet-spinning an acrylonitrile-based precursor to form a coagulated fiber, subjecting the coagulated fiber to primary drawing comprising in-bath drawing, and subjecting the obtained fiber to secondary drawing involving pressurized steam drawing. U.S. Pat. No. 6,641,915 discloses a method for preparing an acrylonitrile fiber for a carbon fiber precursor by spinning an acrylonitrile polymer in a solution to prepare a coagulated fiber, drawing the coagulated fiber from a first coagulation bath, and then stretching the coagulated fiber in a second coagulation bath. Japanese Patent Application Publication No. 1989-052811 discloses a method for preparing an acrylonitrile fiber for a carbon fiber precursor by spinning an acrylonitrile polymer in a solution to prepare a coagulated fiber and drawing the coagulated fiber from a coagulation bath. However, in these techniques, it is difficult to freely control the cross-sectional area of the fiber while achieving mechanical properties as the carbon fiber precursor.

**[0010]** Meanwhile, Korean Patent Application Publication No. 10-1991-0002966 discloses an superdrawn polyethylene fiber reinforced composite material comprising an superdrawn polyethylene fiber and an epoxy resin modified with an elastomer, and Japanese Patent Application Publication No. 2006-265788 discloses a method for producing a composite fiber by melt-spinning a fiber to have a diameter of 1 to 10 μm and then superdrawing the fiber. However, these techniques are to conduct superdrawing to modify the fiber, and the prepared fiber has too low of a carbon yield to be used as the carbon fiber precursor.

**[0011]** The above information disclosed in this Background section is only for enhancement of understanding of the background of the invention and therefore it may contain information that does not form the prior art that is already known in this country to a person of ordinary skill in the art.

### SUMMARY OF THE DISCLOSURE

**[0012]** The present invention provides a method for preparing a precursor fiber for a carbon fiber having excellent properties by spinning a fiber and then preparing a fiber of fine



denier using a superdrawing process. Moreover, the present invention provides a method for preparing a precursor fiber for a carbon fiber, which can prepare a carbon fiber having excellent tensile strength and tensile modulus by reducing the diameter of an as-spun to acrylonitrile fiber extruded from an existing spinneret using a superdrawing process.

**[0013]** Furthermore, the present invention provides a method for preparing a precursor fiber for a carbon fiber, which can prepare a precursor fiber having excellent molecular orientation and reduced diameter and can prepare a carbon fiber having high strength and high stiffness using a superdrawing process.

**[0014]** In one aspect, the present invention provides a method for preparing a precursor fiber for a carbon fiber, the method including: first spinning an acrylonitrile fiber from a spinning dope containing an acrylonitrile polymer; then controlling the fiber diameter by superdrawing the fiber spun; and in response, preparing a precursor fiber by drawing the controlled fiber.

**[0015]** Other aspects and exemplary embodiments of the invention are discussed infra.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0016]** The above and other features of the present invention will now be described in detail with reference to certain exemplary embodiments thereof illustrated the accompanying drawings which are given hereinbelow by way of illustration only, and thus are not limitative of the present invention, and wherein:

**[0017]** FIG. 1 is a schematic process diagram showing a method for preparing an ultrafine carbon fiber disclosed in International Patent Publication No. WO2009/049174; and

**[0018]** FIG. 2 is a schematic process diagram showing a method for preparing a precursor fiber for a carbon fiber in accordance with an exemplary embodiment of the present invention.

**[0019]** It should be understood that the appended drawings are not necessarily to scale, presenting a somewhat simplified representation of various preferred features illustrative of the basic principles of the invention. The specific design features of the present invention as disclosed herein, including, for example, specific dimensions, orientations, locations, and shapes will be determined in part by the particular intended application and use environment.

**[0020]** In the figures, reference numbers refer to the same or equivalent parts of the present invention throughout the several figures of the drawing.

#### DETAILED DESCRIPTION

**[0021]** Hereinafter reference will now be made in detail to various embodiments of the present invention, examples of which are illustrated in the accompanying drawings and described below. While the invention will be described in conjunction with exemplary embodiments, it will be understood that present description is not intended to limit the invention to those exemplary embodiments. On the contrary, the invention is intended to cover not only the exemplary embodiments, but also various alternatives, modifications, equivalents and other embodiments, which may be included within the spirit and scope of the invention as defined by the appended claims.

**[0022]** It is understood that the term “vehicle” or “vehicular” or other similar term as used herein is inclusive of motor

vehicles in general such as passenger automobiles including sports utility vehicles (SUV), buses, trucks, various commercial vehicles, watercraft including a variety of boats and ships, aircraft, and the like, and includes hybrid vehicles, electric vehicles, plug-in hybrid electric vehicles, hydrogen-powered vehicles and other alternative fuel vehicles (e.g., fuels derived from resources other than petroleum). As referred to herein, a hybrid vehicle is a vehicle that has two or more sources of power, for example both gasoline-powered and electric-powered vehicles.

**[0023]** The present invention provides a method for preparing a precursor fiber for a high strength carbon fiber by spinning, superdrawing, and drawing an acrylonitrile fiber, which is shown in the process diagram of FIG. 2.

**[0024]** Preferably, a precursor fiber for a carbon fiber prepared by the present invention is obtained from an acrylonitrile polymer. The acrylonitrile polymer used in an exemplary embodiment of the present invention comprises an acrylonitrile monomer as a main component and is prepared by copolymerization with another monomer. The content of acrylonitrile may be 90 to 99 wt %, more preferably 95 to 99 wt %, with respect to the total weight of the polymer. If the content of the acrylonitrile is less than 90 wt %, the crystalline structures of the carbon fiber precursor and the carbon fiber are not well developed, and thus the strength and stiffness of the carbon fiber may be reduced. In some embodiments the acrylonitrile polymer is prepared by copolymerization with another monomer to reduce the stabilization time and improve the quality of the final carbon fiber. The sum of the content of the acrylonitrile polymer and the content of the acrylonitrile monomer is 100 wt %. Here, the monomer may be one of either an acrylic acid (AA), methacrylic acid (MA), itaconic acid (IA), methacrylate (MA), or acrylamide (AM).

**[0025]** The method of the present invention may include preparing a spinning dope by dissolving an acrylonitrile polymer in a solvent or by solution polymerization to prepare the carbon fiber precursor from the acrylonitrile polymer. Here, the process of dissolving the acrylonitrile polymer in a solvent is more preferable. When a polymer solution prepared by solution polymerization is directly spun, low molecular weight components, initiator, catalyst, etc. may degrade the mechanical properties of the carbon fiber precursor and the carbon fiber. The solvent used in the spinning dope may be either dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and nitric acid. The acrylonitrile polymer spinning dope (hereinafter referred to as the “spinning dope”) contains about 5 to 25 wt %, preferably, 10 to 20 wt % of acrylonitrile polymer. If the content of the polymer is too small, it is difficult to perform the spinning due to low viscosity, whereas, if it is too high, the mechanical properties of the carbon fiber precursor and the carbon fiber may be degraded due to entanglement of acrylonitrile molecules. The spinning dope is kept for more than 24 hours to remove air bubbles, and impurities are removed by a filter having a pore size of less than 10 microns.

**[0026]** In a first step of spinning an acrylonitrile fiber from a spinning dope, the spinning dope is spun in the form of fiber by a typical solution spinning process. Here, a spinneret and a coagulation bath are arranged according to a typical wet-spinning or dry-jet wet spinning (similar to wet spinning except for existing air gap between the spinneret and the coagulation bath) method. Preferably, the air-jet spinning



method improves the orientation of acrylonitrile molecules in the precursor fiber, which leads to the preparation of excellent carbon fiber.

**[0027]** When the spinning dope is spun, the distance between the spinneret and the coagulation bath should be maintained at about 1 to 100 mm, more preferably 5 to 25 mm. A coagulation liquid used in this process is a mixture of a solvent and a non-solvent and, when the content of the non-solvent is higher and when the temperature is higher, the solidification rate is increased. Water or alcohol may be selectively used as the non-solvent.

**[0028]** According to the present invention, in a second step of controlling the fiber diameter by superdrawing the fiber spun in the first step, a superdrawing process is performed on the as-spun fiber prepared by the above process. Here, the superdrawing process is performed at a temperature above the glass transition temperature, preferably at about 100 to 180° C., more preferably at 150 to 170° C. The strain rate is set at about 0.4 to 400 l/sec, preferably at 150 to 250 l/sec. If the strain rate is too high, the orientation of the molecules occurs rapidly, whereas, if the strain rate is too low, the productivity is reduced. Moreover, the superdrawn fiber may have a diameter of about 0.05 to 0.5 denier.

**[0029]** In a third step of preparing a precursor fiber by drawing the fiber controlled and prepared in the second step, a drawing process is performed on the fiber prepared in the second step when the fiber has a desired diameter through the superdrawing process. The drawing process is performed at a temperature of about 150 to 180° C. by a typical method.

**[0030]** As such, when a specific drawing rate is satisfied at a temperature above the glass transition temperature of the polymer by performing the superdrawing process without increasing the oriented crystallization of the crystalline polymer, desirable characteristics can be obtained. According to the present invention, the superdrawing process is performed so that the acrylonitrile precursor fiber produced from a single spinneret is made thin by preventing the oriented crystallization as much as desired, and the drawing process is performed to achieve the final thickness and properties.

**[0031]** According to the prepared precursor fiber of the present invention, the molecular orientation is improved and, in particular, the cross-sectional area of the fiber is reduced by the superdrawing process, which reduces the stabilization time, thereby preparing a carbon fiber having improved strength.

**[0032]** The precursor fiber prepared according to the present invention is used for the preparation of the carbon fiber. Here, the carbon fiber may be prepared under typical stabilization and carbonization conditions, and the stabilization time is set inversely proportional to the cross-sectional area of the fiber.

**[0033]** According to the prepared carbon fiber, the diameter of the as-spun acrylonitrile fiber extruded from an existing spinneret can be reduced to suit its use, thereby preparing a carbon fiber having excellent tensile strength and tensile modulus. Moreover, the carbon fiber prepared using the precursor fiber according to the present invention has excellent properties and thus can be used for the production of vehicle chassis and body parts, aircraft structural materials, wind turbine blades, sporting goods, construction structural materials, etc. When the carbon fiber of the present invention is used as an aircraft structural material, the fuel efficiency can be improved through weight reduction, and the safety can be improved through increased stiffness.

**[0034]** Next, the present invention will be described in more detail with reference to examples. The following examples are provided for a better understanding of the present invention, and the present invention is not limited by the following examples.

#### Example 1

##### Preparation of Precursor Fiber Using Superdrawing

**[0035]** 10 wt % of acrylonitrile polymer prepared by copolymerization with 2 wt % of itaconic acid was dissolved in dimethylsulfoxide and placed in a vacuum oven under reduced pressure to remove air bubbles. Then, an as-spun fiber was prepared by dry-jet wet spinning in which the distance between a spinneret and a coagulation bath was set to 10 mm. In a first coagulation liquid, dimethylsulfoxide and water were mixed in a ratio of 60:40 and, in a second coagulation liquid, a solvent and water were mixed in a ratio of 40:60. A circular spinneret having a diameter of 120  $\mu$ m was used.

**[0036]** The as-spun fiber prepared under the above conditions was subjected to superdrawing at a drawing rate of 200 l/sec using a heating plate or godet roller at a temperature of 150° C. The drawing ratio was the ratio of the winding rate of the superdrawn yarn to the feeding rate of the as-spun fiber and was set to 90 times. The superdrawn yarn was drawn at a drawing rate of 450 l/sec at a temperature of 170° C. The drawing ratio was the ratio of the winding rate of the drawn yarn to the feeding rate of the superdrawn yarn and was set to 15 times.

#### Comparative Example 1

**[0037]** A precursor fiber was prepared in the same manner as Example 1, except that the superdrawing temperature was set at 70° C.

#### Comparative Example 2

**[0038]** A precursor fiber was prepared in the same manner as Example 1, except that the superdrawing rate was set at 380 l/sec.

#### Comparative Example 3

**[0039]** A precursor fiber was prepared in the same manner as Example 1, except that the superdrawing process was not performed.

#### Comparative Example 4

**[0040]** An as-spun fiber having a diameter of 150  $\mu$ m as Example 1, except that the superdrawing process was not performed, was drawn at a drawing rate of 450 l/sec at a temperature of 170° C. and the islands were dissolved, thereby preparing a precursor fiber.

#### Test Example

**[0041]** The tensile strength and tensile modulus of the precursor fiber were measured according to ASTM D3822, in which the gauge length was 25.4 mm and the crosshead speed was 0.254 mm/min. The degree of crystallization was obtained from the ratio of the sum of a crystalline region and an amorphous region of a two-dimensional X-ray diffraction



graph to the area of crystalline areas [(200,110), (201), (310, 020), (003)] using X-ray diffraction. The Herman's orientation factor of polyacrylonitrile (PAN) molecules was calculated using Wilchinsky's method (Wilchinsky, Z. W., MEASUREMENT OF ORIENTATION IN POLYPROPYLENE FILM. Journal of Applied Physics, 1960. 31(11): p. 1969-1972, the content of which are hereby incorporated by reference in its entirety). The fiber diameter was measured by measuring the density of the fiber using a gravimeter, measuring the unit length and the fiber weight, and converting the measured values into the diameter of a circular cross-section yarn based on the following formula:

$$\text{Diameter} = 2 \sqrt{\frac{m}{\pi \rho l}} \text{ (cm)}$$

[0042] where  $m$  represents the weight (g) of the fiber,  $\rho$  represents the density ( $\text{g/cm}^3$ ), and  $l$  represents the fiber length (cm).

[0043] The test results are shown in the following table 1

TABLE 1

Properties	Example 1	Com- parative Exam- ple 1	Com- parative Exam- ple 2	Com- parative Exam- ple 3	Com- parative Exam- ple 4
Tensile strength (GPa)	1.02	0.99	1	0.9	0.8
Tensile modulus (GPa)	27	26	26	24	23
Fiber diameter (μm)	1.1	13.5	3.9	10.4	1.6
Degree of crystallization (%)	67	65	66	63	62
Herman's orientation factor ( $f_{PAN}$ )	0.91	0.82	0.84	0.83	0.87

[0044] Referring to table 1, it can be seen that the fiber diameter was significantly increased in Comparative Example 1 where the superdrawing temperature was low, compared to Example 1. Moreover, it can be seen that the reduction in fiber diameter in Comparative Example 2 where the drawing rate was relatively high was smaller than that of Example 1.

[0045] Furthermore, it can be seen that a precursor fiber having a larger diameter and lower mechanical properties was prepared in Comparative Example 3 where the superdrawing process was not performed, compared to those of Example 1. In addition, it can be seen that a precursor fiber having a smaller diameter and higher mechanical properties could be prepared in Example 1, compared to those of a precursor fiber prepared using an expensive composite spinning machine in Comparative Example 4.

[0046] Therefore, when the precursor fiber is prepared by superdrawing of the illustrative embodiment of the present invention, it is possible to control the fiber diameter according to the superdrawing conditions, thereby preparing a precursor fiber having excellent mechanical properties. The thus pre-

pared precursor fiber can reduce the stabilization and carbonization time during the preparation process of the carbon fiber, thereby reducing the production cost. Moreover, it is possible to prepare a carbon fiber with a well-developed crystalline structure, thereby improving the mechanical properties of the carbon fiber.

[0047] As described above, according to the method for preparing the precursor fiber for a carbon fiber of the illustrative exemplary embodiment of the present invention, the cross-sectional area of the fiber is reduced by the superdrawing process, which reduces the stabilization time, and the carbon fiber with improved strength can be prepared. The thus to prepared carbon fiber can be used for the production of vehicle chassis and body parts, aircraft structural materials, wind turbine blades, sporting goods, construction structural materials, etc. When the carbon fiber of the present invention is used as an aircraft structural material, the fuel efficiency can be improved through weight reduction, and the safety can be improved through increased stiffness.

[0048] The invention has been described in detail with reference to exemplary embodiments thereof. However, it will be appreciated by those skilled in the art that changes may be made in these embodiments without departing from the principles and spirit of the invention, the scope of which is defined in the appended claims and their equivalents.

What is claimed is:

1. A method for preparing a precursor fiber for a carbon fiber, the method comprising:

spinning an acrylonitrile fiber from a spinning dope containing an acrylonitrile polymer;  
in response to spinning, controlling the fiber diameter by superdrawing the fiber spun in the first step; and  
in response, preparing a precursor fiber by drawing the controlled.

2. The method of claim 1, wherein the acrylonitrile polymer is prepared by copolymerization with at least one monomer selected from the group consisting of acrylic acid (AA), methacrylic acid (MA), itaconic acid (IA), methacrylate (MA), and acrylamide (AM).

3. The method of claim 1, wherein the polyacrylonitrile comprises 90 to 99 wt % of acrylonitrile.

4. The method of claim 1, wherein the spinning dope comprises 5 to 25 wt % of acrylonitrile polymer is mixed with a solvent selected from the group consisting of dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and nitric acid.

5. The method of claim 1, wherein the superdrawing is performed at a temperature above the glass transition temperature of the acrylonitrile.

6. The method of claim 5, wherein the superdrawing is performed at a temperature of 100 to 180° C.

7. The method of claim 5, wherein the superdrawing is performed at a strain rate of 0.4 to 400 l/sec

8. A precursor fiber for a carbon fiber prepared by the method of claim 1.

9. The precursor fiber of claim 8, wherein the precursor fiber has a diameter of 0.05 to 0.5 denier.

10. A carbon fiber prepared using the precursor fiber of claim 8.

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