(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 511 450 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
17.07.2019 Bulletin 2019/29

(21) Application number: **17848632.0**

(22) Date of filing: **30.08.2017**

(51) Int Cl.:
D01F 6/18 $^{(2006.01)}$ ***D01F 9/22*** $^{(2006.01)}$

(86) International application number:
PCT/JP2017/031124

(87) International publication number:
WO 2018/047692 (15.03.2018 Gazette 2018/11)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **12.09.2016 JP 2016177277**

(71) Applicant: **Toray Industries, Inc.**
Tokyo 103-8666 (JP)

(72) Inventors:
- **KAJIWARA, Kentaro**
  Otsu-shi
  Shiga 520-8558 (JP)
- **HORINOUCHI, Ayanobu**
  Otsu-shi
  Shiga 520-8558 (JP)
- **OKUDA, Haruki**
  Iyo-gun
  Ehime 791-3193 (JP)
- **NOGUCHI, Tomohisa**
  Iyo-gun
  Ehime 791-3193 (JP)
- **WATANABE, Fumitaka**
  Otsu-shi
  Shiga 520-8558 (JP)

(74) Representative: **Mewburn Ellis LLP**
City Tower
40 Basinghall Street
London EC2V 5DE (GB)

(54) COAGULATED YARN AND MANUFACTURING METHOD THEREOF, CARBON FIBER PRECURSOR FIBER, AND METHOD FOR MANUFACTURING CARBON FIBER

(57) Provided are a coagulated yarn for obtaining carbon fiber having high strength, a carbon fiber precursor fiber using same, and carbon fiber using same. The coagulated yarn, which is used for manufacturing carbon fiber, is a coagulated yarn the surface hole diameter of which is 30 nm or less and the degree of swelling is less than 100% or a coagulated yarn the surface hole diameter of which is 30 nm or less and the inner hole diameter is 30 nm or less. The carbon fiber precursor fiber and the carbon fiber are obtained using such a coagulated yarn.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a carbon fiber suitable for use in aircraft members, automobile members, and ship members as well as the applications of sport gears such as golf shaft and fishing rod and other general industrial applications.

Background Art

[0002] Carbon fibers have a low specific weight simultaneously with a high specific strength and a high specific modulus, and accordingly, they have been widely used in the sports and aerospace applications as a reinforcement fiber for composite materials. Carbon fibers have recently extended their use to automobile applications, civil engineering and building applications, pressure vessels, windmill blades, and the like, and there is a demand for further improvement in their performance.

[0003] Performance of the carbon fiber is known to greatly depend on the performance of the precursor fiber for carbon fiber. In particular, surface irregularities in the surface layer of the precursor fiber for carbon fiber are conceived to induce loss of carbon fiber strength, and a dry-wet spinning method which is more likely to form a smooth surface has been proposed. However, a technology capable of further improving the strength is widely investigated.

[0004] For example, Patent Document 1 proposes a technology wherein intrusion of an oil agent is suppressed by controlling the conditions of the dry-wet spinning step and stretching-in-the bath step by the use of a water-base coagulation bath for densification of the surface layer part.

[0005] Patent Document 2 proposes a technology wherein the size of the voids in the coagulated yarn is reduced by conducing the dry-wet spinning in a coagulation bath comprising a paraffin hydrocarbon.

[0006] Patent Document 3 proposes a technology having characteristic feature in the coagulation step. More specifically, the technology proposed in the Patent Document 3 is the one wherein a polymer solution of low concentration is gelated in a low temperature coagulation bath of an alcohol and speed in the stretching step is increased by high draw ratio to improve the productivity.

Prior Art Documents

Patent Documents

[0007]

Patent Document 1: WO2010/143680
Patent Document 2: Japanese Unexamined Patent Publication (Kokai) No. HEI 2-74607
Patent Document 3: Japanese Unexamined Patent Publication (Kokai) No. 2010-100970

Summary of the Invention

Problems to Be Solved by the Invention

[0008] While the effect of improving the carbon fiber strength is realized by the use of the coagulated yarn produced by densifying the surface layer described in Patent Document 1 and the coagulated yarn having reduced voids described in Patent Document 2, the effect has been insufficient.

[0009] Patent Document 1 discloses that the stretching of the coagulated yarn having the degree of swelling of up to 160% under particular conditions is preferable, and the case of stretching the yarn having a degree of swelling of 100 to 155% is disclosed in the Examples. However, in the investigation of the inventors of the present invention, it has been found that increase in the strength is insufficient when the degree of swelling is 100% or higher. Patent Document 2 discloses the technology where the degree of swelling had been reduced. However, in the investigation of the inventors of the present invention, it has been found that, when the proportion of the paraffin hydrocarbon is increased for reducing the degree of swelling, the carbon fiber had low evenness and the surface layer had an increased pore size, and the effect of improving the strength had been limited despite the decrease in the degree of swelling conceivably because of the slow coagulation rate. With regard to the technology of the Patent Document 3, this technology certainly had the effect of improving the productivity while it did not necessarily have the effect of improving the strength probably because of the difficulty of achieving the densification necessary to realize the high strength in the coagulation step due to the low polymer concentration of the polymer solution.

[0010] An object of the present invention is to provide a coagulated yarn for producing a carbon fiber having a high strength, a precursor fiber for carbon fiber, and a carbon fiber prepared by using these.

Means for Solving the Problems

[0011] In order to solve the problems as described above, the coagulated yarn of the present invention has a pore size of the surface layer of 30 nm or less and a degree of swelling of less than 100%, or a pore size of the surface layer of 30 nm or less and a pore size of the inner layer of 30 nm or less.

Advantageous Effects of the Invention

[0012] The coagulated yarn of the present invention has a pore size of the surface layer of 30 nm or less and a degree of swelling of less than 100%, or a pore size of the surface layer of 30 nm or less and a pore size of the inner layer of 30 nm or less, and such constitution enables production of a precursor fiber for carbon fiber which is capable of producing a carbon fiber having a high strength and a carbon fiber having a high strength.

Brief Description of the Drawings

[0013]

FIG. 1 is an image of the surface layer of the coagulated yarn of Example 1 taken by TEM.
FIG. 2 is an image of the inner layer of the coagulated yarn of Example 1 taken by TEM.
FIG. 3 is an image of the surface layer of the coagulated yarn of Comparative Example 1 taken by TEM.
FIG. 4 is an image of the inner layer of the coagulated yarn of Comparative Example 1 taken by TEM. Description of Preferred Embodiments

[0014] In the present invention, a carbon fiber having a high strength is produced by controlling pore size of the surface layer of a coagulated yarn to a small size and also controlling the degree of swelling to an extremely low level. In another embodiment, a carbon fiber having a high strength is produced by controlling the pore size of the surface layer of a coagulated yarn to a small size and also controlling pore size of the inner layer to a small size.

[0015] The precursor fiber for carbon fiber as used in the present invention is a precursor fiber that can be produced into carbon fiber. An exemplary such precursor fiber for carbon fiber is the one produced by stretching the coagulated yarn.

[Coagulated yarn]

(Pore size of the surface layer of the coagulated yarn)

[0016] The size of the surface layer pores in the coagulated yarn of the present invention is 30 nm or less. The strength of the yarn will be higher when this size is smaller, and the pore size of the surface layer is preferably up to 20 nm and more preferably up to 10 nm. When the pore size of the surface layer is up to 1 nm, desolvation in the washing with water will take time, and therefore, the lower limit is approximately 1 nm. In view of the balance between the carbon fiber strength and processability, the pore size of the surface layer is preferably 1 nm to 10 nm.

[0017] The surface layer as used in the present invention corresponds to the area in the periphery (in the range of up to 500 nm from the exterior periphery to the interior) of the cross section in the direction of the fiber diameter. The pore size is the size of the pore formed by the fibrillar structure of the coagulated yarn and voids in the fibrillar structure.

(Degree of swelling of the coagulated yarn)

[0018] In an aspect of the present invention, the degree of swelling of the coagulated yarn is less than 100%. When the pore size of the surface layer is within the range as described above, the strength will increase with the decrease in the degree of swelling, and therefore, the degree of swelling is preferably less than 90%, and more preferably less than 85%. When the degree of swelling is up to 3%, desolvation by washing with water will be retarded, and therefore, the lower limit is approximately 3%. The degree of swelling is more preferably 3% to 85% in view of the balance between the carbon fiber strength and processability.

(Pore size of the inner layer of the coagulated yarn)

[0019] In another aspect of the present invention, the pore size of the inner layer of the coagulated yarn is 30 nm or less. When the pore size of the surface layer is within such range, the strength will increase with the decrease in the pore size of the inner layer, and accordingly, the pore size of the inner layer is preferably up to 20 nm, and more preferably up to 10 nm. When the pore size of the inner layer is up to 1 nm, desolvation in the washing with water will take time, and therefore, the lower limit is approximately 1 nm. In view of the balance between the carbon fiber strength and processability, the pore size of the inner layer is preferably 1 nm to 10 nm.

[0020] The inner layer as used in the present invention corresponds to the circular area (with the diameter of up to 500 nm) concentric with the cross section of the fiber in the direction of the fiber diameter. The pore size is the size of the pore formed by the fibrillar structure of the coagulated yarn and voids in the fibrillar structure.

[Production method of the coagulated yarn]

[0021] The coagulated yarn of the present invention can be produced, for example, by the process comprising the step of polymer coagulation using a coagulation bath prepared by mixing a non-solvent having a solubility parameter of -11 to + 20 in relation to the solubility parameter of polymer for forming the coagulated yarn and solvent of the polymer solution for forming the coagulated yarn at a non-solvent to solvent ratio of 1:9 to 9:1.

[0022] In the present invention, preferably, the polymer solution is ejected from the spinneret in the spinning step, introduced in the coagulation bath in the coagulation step for precipitation of the polymer to form the coagulated yarn, washed with water, stretched in the bath, applied with an oil agent in the oil agent-application step, and dried in the drying step to thereby produce the precursor fiber for carbon fiber. The coagulated yarn of the present invention may also be produced by wet spinning or dry-wet spinning of the polymer solution. In such process, the pore size and the degree of swelling may be controlled by the conditions used in the coagulation of the polymer solution in the coagulation bath, namely, the conditions used for precipitating the polymer in the polymer solution from the solvent.

(Spinning step)

[0023] The spinning method used may be either wet spinning or dry-wet spinning. In the present invention, however, the temperature of the coagulation bath is preferably set at a low temperature as will be described below. In the meanwhile, in consideration of the spinnability, the polymer solution should also be at a temperature capable of realizing certain flowability. Accordingly, a difference in the temperature is often set between the temperature of the coagulation bath and the temperature of the polymer solution. Therefore, use of the dry-wet spinning is preferable in view of the ease of setting temperature difference between the coagulation bath and the polymer (temperature of the polymer ejection spinneret).

[0024] The polymer used in the present invention is not particularly limited as long as it can be made into a carbon fiber. Examples include polyacrylonitrile, a copolymer containing polyacrylonitrile as its main component, and a mixture containing polyacrylonitrile as its main component. Unless otherwise noted, a copolymer containing polyacrylonitrile as its main component is called "polymer" in the present invention.

[0025] The solvent for the polymer is not particularly limited as long as the polymer is soluble in the solvent, and examples include dimethyl sulfoxide, dimethylformamide, and dimethyl acetamide.

[0026] Although concentration of the polymer in the polymer solution is not particularly limited, the concentration is preferably at least 10% by weight since the degree of swelling is likely to be reduced with the increase in the polymer concentration. The upper limit is not particularly limited as long as the polymer is soluble in the solvent, and the upper limit is generally up to 30% by weight. Often, a higher polymer concentration is also preferable in view of reducing the pore size.

[0027] The polymer solution is more likely to be flowable when the temperature of the polymer solution ejected from the spinneret is higher. On the other hand, the precipitation in the coagulation bath is easier when the polymer solution is at a lower temperature. When the polymer precipitation in the coagulation bath is facilitated, the pore size will be smaller since the pore size will not be developed in the liquid-liquid phase separation process. Accordingly, the polymer solution preferably has a temperature of 15 to 95°C.

(Coagulation step)

[0028] The coagulated yarn of the present invention can be produced, for example, by the process comprising the step of polymer coagulation using a coagulation bath prepared by mixing a non-solvent having a solubility parameter of -11 to + 20 in relation to the solubility parameter of polymer for forming the coagulated yarn and a solvent of the polymer solution for forming the coagulated yarn at a non-solvent to solvent ratio of 1:9 to 9:1. The solubility parameter as used in the present invention is Hansen solubility parameter ($MPa^{0.5}$).

[0029] The polymer is less soluble when difference between the solubility parameter of the non-solvent and the solubility parameter of the polymer is large. In the present invention, it has been discovered that the degree of swelling and the pore size of inner layer can be reduced by choosing a non-solvent having a solubility parameter near that of the polymer. The solubility parameter of the non-solvent is preferably -9 to + 15, and more preferably - 7 to + 10 in relation to the solubility parameter of the polymer. When polyacrylonitrile is used for the polymer, the solubility parameter of the polyacrylonitrile is 27.4 and the preferable solubility parameter of the non-solvent is 16.4 to 47.4. Examples of such non-solvent include methanol, ethanol, propanol, butanol, glycerin, ethylene glycol, propylene glycol, butanediol, acetic acid, ethyl acetate, acetone, benzene, toluene, xylene, cyclohexane, methyl ethyl ketone, and chloroform. The non-solvent as used herein is those wherein the polymer is precipitated upon addition of the polymer solution under the environment of normal pressure and normal temperature. The solubility parameter used is the value described in or calculated by the method described in a handbook (see, for example, Hansen Solubility Parameters A User's Handbook Second Edition, CRC Press (2007)). When the polymer is a mixture, difference between the solubility parameter (δ) of the non-solvent and the solubility parameter of each polymer are compared, and a non-solvent having a solubility parameter which is -11 to + 20 in relation to the solubility parameter of at least one polymer is used. When the non-solvent is a mixture, 3 parameters, namely, dispersion forces (δ_d), dipolar intermolecular force (δ_p), and hydrogen bond (δ_h) are calculated by the addition corresponding to the volume fraction of the mixture, and the square root of the total sum of the square of each of the resulting 3 parameters is used for the solubility parameter of the non-solvent.

[0030] For example, when the non-solvent is a two-component mixture comprising non-solvents A and B, δ_d, δ_p, and δ_h of the mixed non-solvent are

[Mathematic formula 1]

$$[\delta_d, \delta_p, \delta_h] = [(\phi_A \cdot \delta_{dA} + \phi_B \cdot \delta_{dB}), (\phi_A \cdot \delta_{pA} + \phi_B \cdot \delta_{pB}), (\phi_A \cdot \delta_{hA} + \phi_B \cdot \delta_{hB})]$$

wherein φ_A and φ_B are volume fraction of the mixture, and $\varphi_A + \varphi_B = 1$. The solubility parameter (δ) of the mixed non-solvent can be calculated from the calculated δ_d, δ_p, and δ_h of the mixed non-solvent by:

[Mathematic formula 2]

$$\delta = \sqrt{(\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2}$$

[0031] The inventors of the present invention have also discovered that the pore size of the surface layer and the inner layer can be controlled by mixing a solvent for the polymer in the coagulation bath. In addition, the inventors of the present invention have discovered that while circularity tended to decrease when the non-solvent in the range as described above was used, increase of the polymer solvent had the effect of increasing the circularity while retaining the low degree of swelling. On the other hand, it has also been found that the pore size of the surface layer and the inner layer can be reduced by reducing the amount of the polymer solvent. In one aspect of the present invention, the ratio of the non-solvent to solvent is more preferably 2:8 to 8:2, still more preferably 3:7 to 7:3, and most preferably 4:6 to 6:4. In addition, other substances may be present to the extent not adversely affecting the merits of the present invention. It is to be noted that, the ratio as used herein is the ratio in weight.

[0032] The diffusion coefficient D of the non-solvent in the coagulation bath of the present invention is preferably up to 3.4×10^{-10} $m^2 \cdot S^{-1}$. When the diffusion coefficient D is low, the resulting coagulated yarn will exhibit a lower degree of swelling and the surface and inner layers will have a smaller pore size. The diffusion coefficient D of the non-solvent is the coefficient obtained by pulsed magnetic field gradient nuclear magnetic resonance (PFG-NMR method). In the PFG-NMR, diffusion movement distance of the substance, namely, information on the position of the nuclear spin can be collected by applying a pulsed magnetic field gradient (PFG) in the direction of the static magnetic field in the ordinary NMR analysis.

[0033] More specifically, this method is a method wherein attenuation of the observed peak strength based on the change of the PFG strength is tracked, and the diffusion coefficient is determined from the gradient obtained by exponential function analysis of the attenuation change. In the actual measurement of the non-solvent diffusion coefficient D using the PFG-NMR, an NMR system equipped with Diff60 probe (AVANCE III HD 400 manufactured by Bruker Biospin) is used, and the evaluation was conducted by Stejskal-Tanner equation:

$$\ln(I/I_0) = -D\gamma^2 G^2 \alpha^2 (\Delta - \alpha/3)$$

wherein G is intensity of magnetic field gradient, α is pulse width of magnetic field gradient, Δ is interval of the magnetic field gradient pulse (diffusion time), and γ is nuclear gyromagnetic ratio of the observing nucleus. $\ln(I/I_0)$ which is the signal strength I standardized with the signal strength I_0 when G is minimum is plotted in relation to the $G^2\gamma^2\alpha^2(\Delta-\alpha/3)$, and the diffusion coefficient D of the non-solvent is determined from the gradient non-solvent. When two or more types of non-solvents are included, the D of the non-solvent having the highest diffusion coefficient D (the non-solvent with the highest diffusion speed) was defined as the D of the coagulating liquid.

[0034] The coagulation bath in the present invention preferably has a viscosity of 2 to 1000 mPa·s. When the coagulation bath has a high viscosity, the degree of swelling is likely to be low, while low viscosity of the coagulation bath facilitates precipitation of the polymer and decrease of the pore size. The viscosity of the coagulation bath is more preferably 5 to 500 mPa·s, and still more preferably 10 to 200 mPa.

[0035] In the coagulation bath of the present invention, temperature of the coagulation bath is preferably 10 to 100°C lower than the temperature of the polymer ejected from the spinneret. When the temperature of the coagulation bath is low, polymer precipitation is promoted, and the pore size can be controlled to a smaller size. On the other hand, when the coagulation bath has a high temperature, spinnability will be improved, and production of fibers with reduced fluffs and fiber-fiber adhesion will be enabled. The temperature of the coagulation bath is preferably 20 to 80°C, more preferably 30 to 60°C lower than the temperature of the polymer solution.

[Production method of the precursor fiber for carbon fiber]

[0036] Next, the method for producing the precursor fiber for carbon fiber of the present invention is described.

[0037] In the present invention, the production method of the precursor fiber for carbon fiber preferably comprises forming the coagulated yarn by the method as described above and conducting the stretching step. More preferably, the precursor fiber for carbon fiber is produced by washing the coagulated yarn with water, stretching the washed yarn in the bath, applying an oil agent, and drying the yarn. In another preferable embodiment, the method may further comprise a dry heat stretching step or a steam stretching step. The fiber after the coagulation may be directly subjected to the stretching in the bath without conducting the step of washing with water, or the fiber may be subjected to the stretching in the bath after removing the solvent by the washing with water.

[0038] After the stretching step in the bath, a silicone oil agent is preferably applied to the stretched fibers in order to prevent adhesion between the filaments.

[0039] After applying the oil agent, the fibers are preferably dried. In addition, after the drying step, the fibers are preferably stretched in a heated medium for the purpose of improving the productivity or orientation parameter of crystallites. Examples of the preferable heated medium include steam under pressure and superheated steam in view of the stable operation and the cost.

[0040] When the draw ratio is high, arrangement of the molecules in the fiber axis direction is promoted, and the tensile strength after production into the carbon fiber is more likely to be improved. On the other hand, when the draw ratio is reduced, improvement in the evenness in the fiber longitudinal direction is more likely to be becomes easier. Accordingly, the total draw ratio is preferably at least 1 and less than 20.

[Production method of the carbon fiber]

[0041] Next, the method for producing the carbon fiber of the present invention is described.

[0042] In the present invention, the production method of the carbon fiber preferably comprises the steps of producing the precursor fiber for carbon fiber and subjecting the precursor fiber for carbon fiber to a heat treatment. The heat treatment step is not particularly limited as long as the precursor fiber for carbon fiber is heated in the production of the carbon fiber from the precursor fiber for carbon fiber. Examples of such step include the stabilization (oxidation) or fireproofing step, pre-carbonization step, carbonization step, and graphitization step as described below.

[0043] In the present invention, preferably, the precursor fiber for carbon fiber produced as described above is sequentially subjected to a stabilization step wherein the fibers are made fireproof in the air at a temperature of 200 to 300°C, a pre-carbonization step wherein the fibers produced by the stabilization step is preliminarily carbonized in an inert atmosphere at a temperature of 300 to 800°C, and a carbonization step wherein the fibers produced by the pre-carbonization step are carbonized in an inert atmosphere at a temperature of 1,000 to 3,000°C to produce the carbon fiber.

[0044] When a carbon fiber having a higher modulus is desired, graphitization may be conducted subsequent to the carbonization step. The temperature of the graphitization step is preferably 2,000 to 2,800°C, and the maximum temperature may be adequately selected depending on the properties required for the intended carbon fiber. The draw ratio in the graphitization step may be adequately selected depending on the properties required for the intended carbon fiber so that the quality loss such as fluff generation will not be caused.

(Surface modification step)

[0045] The resulting carbon fiber may be subjected to electrolytic treatment for the surface modification so that the fiber reinforced composite material obtained by the electrolytic treatment will exhibit adequate adhesion between the carbon fiber and the carbon fiber matrix. This will solve the problems such as brittle fracture of the composite material by the excessively high adhesion, loss of tensile strength in the fiber direction, and failure to develop the strength properties in the non-fiber direction due to high tensile strength in the fiber direction but with poor adhesion with the resin. As a consequence, the resulting fiber reinforced composite material will exhibit well-balanced strength properties in both fiber direction and non-fiber direction.

[0046] After the electrolytic treatment, sizing process may be conducted to provide convergency with the carbon fiber. The sizing agent may be an adequately selected sizing agent having good compatibility with the matrix resin depending on the type of the resin used.

Examples

[0047] The data in the Examples and the Comparative Examples were measured by the procedures as described below.

1. Pore size of the coagulated yarn

(1) Sample preparation

[0048] The liquid in the coagulated yarn was replaced with water, and after freeze drying, this yarn was embedded in a resin. Sections of 100 nm were prepared with an ultramicrotome.

(2) Observation

[0049] After removing the resin in the prepared section, the section was observed by using a transmission electron microscope at an acceleration voltage of 100 kV. The cross-section in the fiber diameter direction was observed at a magnification of 10,000.

(3) Measurement of the pore size

[0050]

A. Noise was removed by Image Processing Software J Trim ver.1.53c (J Trim) at the applied intensity of 50.
B. Normalization of the histogram for the image obtained in A was conducted with the J Trim.
C. Black and white conversion was conducted by using 145 for the border threshold for the image obtained in B by the J Trim.
D. In the image obtained in C, necessary areas were selected with an area selection tool of Image Processing Software Image J 1.50i (Image J) (the area with the width of 500 nm from the outer periphery was selected for the surface layer, and the circular area having a diameter of 500 nm wherein the center was the center of gravity of the cross-section was used for the inner layer).
E. For the image obtained in D, the area of the part corresponding to the pore was measured by particle analyzing command of the Image Processing Software Image J 1.50i (Image J), and the thus obtained area was converted to a circle to determine the particle size.
F. Of the particle size obtained in the image obtained in E, average of the second largest to the 31st largest was used for the particle size. When 31 particles were not detected, the values in the detected range were used.

2. Degree of swelling of the coagulated yarn

[0051] First, about 10 g of the coagulated yarn was sampled, and washed with water for at least 12 hours. Next, the yarn was dehydrated by using a centrifugal dehyhdrator (for example, H-110A manufactured by Kokusan) at 3000 rpm for 3 minutes and fiber weight after the dehydration was determined. Subsequently, the dehydrated sample was dried in a dryer adjusted to 105°C for 2.5 hours, and the fiber weight after the drying was determined. The degree of swelling of the fiber was calculated by the following equation.

Equation: degree of fiber swelling (%) = ((fiber weight after the water removal − fiber weight after the drying)/fiber weight after the drying)) x 100

3. Tensile strength and modulus of the carbon fiber bundle

[0052] The value was determined on the bases of JIS R7608 (2007) "Carbon fiber: Determination of tensile properties of resin-impregnated yarn". The resin-impregnated strand of the carbon fiber to be measured was prepared by impregnating carbon fiber or graphitized fiber with 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexyl-carboxylate (100 parts by weight) / boron trifluoride monoethylamine (3 parts by weight) / acetone (4 parts by weight) and curing at a temperature of 130°C for 30 minutes. The number of carbon fiber strand measured was 6, and the average of the measurements was used for the tensile strength. In the Example, "Bakelite" (Registered Trademark) ERL4221 manufactured by Union Carbide was used for the 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexyl-carboxylate.

4. Measurement of the diffusion coefficient (D) of the non-solvent

[0053] The diffusion coefficient (D) of the non-solvent in each coagulation bath was measured by PFG-NMR method using NMR system (AVANCE III HD400 manufactured by Bruker Biospin) equipped with Diff60 probe. The measurement was conducted at a temperature of 5°C.

(Example 1)

[0054] A copolymer comprising acrylonitrile and itaconic acid was polymerized by solution polymerization using dimethyl sulfoxide for the solvent and using a polymerization initiator. The resulting polyacrylonitrile copolymer was used for the spinning dope solution.

[0055] The spinning dope solution was controlled to 50°C, and after ejecting into air, it was introduced in a coagulation bath prepared by mixing at 48% by weight of dimethyl sulfoxide (polymer solvent) and 52% by weight of ethylene glycol (non-solvent) controlled to 5°C, and the coagulated fiber was produced by dry-wet spinning by taking up at a speed corresponding to a spinning draft of 2.5. The coagulated fiber was washed with water and stretched in water bath. Subsequently, an amino-modified silicone-based silicone oil agent was applied to the fiber bundle that had been stretched in water bath, and the drying densification process was conducted by using a heater roller, and stretched in a steam at elevated pressure to a total draw ratio of the process of 10 to produce a polyacrylonitrile precursor fiber for carbon fiber having a filament fineness of 0.8 dtex. Next, the resulting polyacrylonitrile precursor fiber for carbon fiber was subjected to stabilization process in the air having a temperature gradient of 220 to 270°C to produce a stabilized bundle of fibers. The resulting stabilized bundle of fibers was subjected to preliminary carbonization treatment in nitrogen atmosphere at a temperature of 300 to 800°C to produce a bundle of preliminarily carbonized fibers. The resulting bundle of preliminarily carbonized fibers was subjected to carbonization treatment in nitrogen atmosphere at the maximum temperature of 1400°C. Subsequently, the fiber was subjected to electrolytic surface treatment by using aqueous solution of sulfuric acid for the electrolyte, washed with water, and dried, and carbon fiber was obtained after applying a sizing agent.

(Example 2)

[0056] The procedure of Example 1 was repeated except that methanol was used for the non-solvent in the coagulation bath to obtain the carbon fiber.

(Example 3)

[0057] The procedure of Example 1 was repeated except that temperature of the coagulation bath was controlled to 45°C.

(Example 4)

[0058] The procedure of Example 1 was repeated except that n-butanol was used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber.

(Example 5)

[0059] The procedure of Example 1 was repeated except that glycerin and ethanol were used for the non-solvent in the coagulation bath to obtain the carbon fiber.

(Example 6)

[0060] The procedure of Example 1 was repeated except that dimethylformamide was used for the polymer solvent to obtain the carbon fiber.

(Example 7)

[0061] The procedure of Example 1 was repeated except that ethylene glycol and ethanol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber.

(Example 8)

[0062] The procedure of Example 1 was repeated except that propylene glycol and ethanol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber.

(Example 9)

[0063] The procedure of Example 1 was repeated except that water and glycerin were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 2.7×10^{-10} $m^2 \cdot S^{-1}$.

(Example 10)

[0064] The procedure of Example 1 was repeated except that water and ethylene glycol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 2.7×10^{-10} $m^2 \cdot S^{-1}$.

(Example 11)

[0065] The procedure of Example 10 was repeated except that temperature of the coagulation bath was controlled to 25°C.

(Example 12)

[0066] The procedure of Example 10 was repeated except that temperature of the coagulation bath was controlled to - 15°C.

(Example 13)

[0067] The procedure of Example 1 was repeated except that water and propylene glycol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 3.3×10^{-10} $m^2 \cdot S^{-1}$.

(Example 14)

[0068] The procedure of Example 1 was repeated except that water and methanol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 4.4×10^{-10} $m^2 \cdot S^{-1}$.

(Example 15)

[0069] The procedure of Example 1 was repeated except that water and ethanol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 3.4 x 10^{-10} $m^2 \cdot S^{-1}$.

(Example 16)

[0070] The procedure of Example 1 was repeated except that water and 1-propanol were used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 5.3 x 10^{-10} $m^2 \cdot S^{-1}$.

(Comparative Example 1)

[0071] The procedure of Example 1 was repeated except that water was used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 3.5 x 10^{-10} $m^2 \cdot S^{-1}$.

(Comparative Example 2)

[0072] The procedure of Example 1 was repeated except that no polymer solvent was used in the coagulation bath to obtain the carbon fiber.

(Comparative Example 3)

[0073] The procedure of Example 1 was repeated except that liquid paraffin and decanol were used for the non-solvent and no polymer solvent was used in the coagulation bath to obtain the carbon fiber. The type and the combination of the non-solvent used were the same as the examples described in Patent Document 2. The resulting coagulated yarn had a pore size of the surface layer of 42 nm which was outside the scope of claims 1 to 3.

(Comparative Example 4)

[0074] The procedure of Example 1 was repeated except that water was used for the non-solvent and dimethylformamide was used for the polymer solvent in the coagulation bath, and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The type of the non-solvent, the type of the solvent, and the mixing ratio used were the same as the examples described in Patent Document 1. The resulting coagulated yarn had a pore size of the surface layer of 35nm and a degree of swelling of 108%, which were outside the range of claims 1 to 3. The D evaluated by the PFG-NMR was 5.5 x 10^{-10} $m^2 \cdot S^{-1}$.

(Comparative Example 5)

[0075] The procedure of Example 1 was repeated except that water was used for the non-solvent in the coagulation bath and ratio of the non-solvent to the polymer solvent was changed to obtain the carbon fiber. The D evaluated by the PFG-NMR was 5.8 x 10^{-10} $m^2 \cdot S^{-1}$.

[Table 1-1]

[0076]

[Table 1-1]

	Production conditions								Physical properties				
	Non-solvent (1)		Non-solvent (2)		Non-solvent (total)	Solvent	Mixing ratio (Weight fraction)	Viscosity of the coagulation bath	Temperature difference between the polymer solution and the coagulation bath	Coagulated yarn			Carbon fiber
	-	Solubility parameter	-	Solubility parameter	Solubility parameter	-	Non-solvent (1) /non-solvent (2)/ solvent			Pore size of the surface layer	Pore size of the inner layer	Degree of swelling	Strength
	-	$(MPa)^{0.5}$	-	$(MPa)^{0.5}$	$(MPa)^{0.5}$	-	-	mPa·s	°C	nm	nm	%	GPa
Example 1	Ethylene glycol	33			33	DMSO	52/0/48	17	45	3	3	82	8.9
Example 2	Methanol	29.6			29.6	DMSO	52/0/48	10	45	12	15	85	8.5
Example 3	Ethylene glycol	33			33	DMSO	52/0/48	17	5	15	3	84	8.5
Example 4	n-butanol	23.2			23.2	DMSO	40/0/60	15	45	7	10	83	8.7
Example 5	Glycerine	36.2	Ethanol	26.5	30.2	DMSO	26/26/48	50	45	4	18	82	8.7
Example 6	Ethylene glycol	33			33	DMF	52/0/48	15	45	5	5	80	8.7
Example 7	Ethylene glycol	33	Ethanol	26.5	27.7	DMSO	20/60/20	16	45	9	7	85	8.7
Example 8	Propylene glycol	30.2	Ethanol	26.5	27.3	DMSO	20/60/20	14	45	12	7	87	8.5
Example 9	Water	47.8	Glycerine	36.2	39.5	DMSO	20/60/20	20	45	8	5	85	8.7
Example 10	Water	47.8	Ethylene glycol	33	36.8	DMSO	20/60/20	18	45	19	10	88	8.5

[Table 1-2]

[0077]

[Table 1-2]

	Production conditions								Physical properties				
	Non-solvent (1)		Non-solvent (2)		Non-solvent (total)	Solvent	Mixing ratio (Weight fraction)	Viscosity of the coagulation bath	Temperature difference between the polymer solution and the coagulation bath	Coagulated yarn			Carbon fiber
	-	Solubility parameter	-	Solubility parameter	Solubility parameter	-	Non-solvent (1) /non-solvent (2) /solvent			Pore size of the surface layer	Pore size of the inner layer	Degree of swelling	Strength
	-	$(MPa)^{0.5}$	-	$(MPa)^{0.5}$	$(MPa)^{0.5}$	-	-	mPa·s	°C	nm	nm	%	GPa
Example 11	Water	47.8	Ethylene glycol	33	36.8	DMSO	20/60/20	18	25	21	12	90	8.3
Example 12	Water	47.8	Ethylene glycol	33	36.8	DMSO	20/60/20	18	65	17	8	84	8.3
Example 13	Water	47.8	Propylene glycol	30.2	33.9	DMSO	20/60/20	14	45	19	12	90	8.4
Example 14	Water	47.8	Methanol	29.6	33.2	DMSO	20/60/20	7	45	28	19	96	8.2
Example 15	Water	47.8	Ethanol	26.5	30.6	DMSO	20/60/20	9	45	26	21	92	8.3
Example 16	Water	47.8	1-Propanol	24.6	29.0	DMSO	20/60/20	7	45	22	20	98	8.1
Comparative Example 1	Water	47.8			47.8	DMSO	20/0/80	8	45	32	50	102	8
Comparative Example 2	Ethylene glycol	33			33	(DMSO)	100/0/0	16	45	40	3	85	7.5
Comparative Example 3	Liquid paraffin	16.2	1-decanol	19.4	16.4	(DMSO)	90/10/0	70	45	42	3	80	7.7
Comparative Example 4	Water	47.8			47.8	DMF	20/0/80	7	45	35	42	108	7.7
Comparative Example 5	Water	47.8			47.8	DMSO	50/0/50	7	45	48	62	131	7.1

Claims

1. A coagulated yarn used for producing a precursor fiber for carbon fiber wherein pore size of the surface layer is 30 nm or less and degree of swelling is less than 100%.

2. A coagulated yarn used for producing a precursor fiber for carbon fiber wherein pore size of the surface layer is 30 nm or less and pore size of the inner layer is 30 nm or less.

3. A coagulated yarn according to claim 1 wherein the pore size of the surface layer is 30 nm or less and pore size of the inner layer is 30 nm or less.

4. A method for producing a coagulated yarn according to any one of claims 1 to 3 comprising the step of coagulating the polymer using a coagulation bath prepared by mixing a non-solvent having a solubility parameter of -11 to + 20 in relation to the solubility parameter of the polymer for forming the coagulated yarn and a solvent of the polymer for forming the coagulated yarn at a non-solvent to solvent ratio of 1:9 to 9:1.

5. A method for producing a coagulated yarn according to claim 4 using a coagulation bath wherein the non-solvent has a diffusion coefficient of up to 3.4×10^{-10} $m^2 \cdot S^{-1}$.

6. A method for producing a coagulated yarn according to claim 4 or 5 wherein the coagulation bath has a viscosity of 2 to 1000 mPa·s.

7. A method for producing a coagulated yarn according to any one of claims 4 to 6 wherein the coagulation bath has a temperature 10 to 100°C lower than the temperature of the polymer solution.

8. A method for producing a coagulated yarn according to any one of claims 4 to7 further comprising the step of spinning at a spinning draft of 1 to 20.

9. A method for producing precursor fiber for carbon fiber comprising the step of stretching the coagulated yarn according to any one of claims 1 to 3.

10. A method for producing precursor fiber for carbon fiber comprising the steps of obtaining a coagulated yarn by the method for producing a coagulated yarn according to any one of claims claim 4 to 8 and stretching the coagulated yarn.

11. A method for producing a carbon fiber comprising the steps of producing a precursor fiber for carbon fiber by the method for producing a precursor fiber for carbon fiber according to claim 9 or 10 and subjecting the precursor fiber for carbon fiber to a heat treatment.

Figure 1

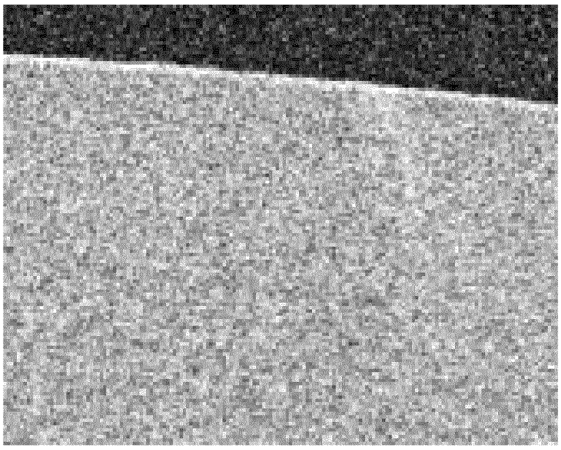


Figure 2

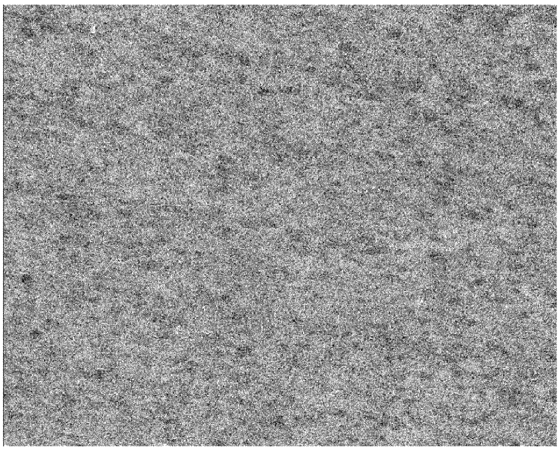


Figure 3

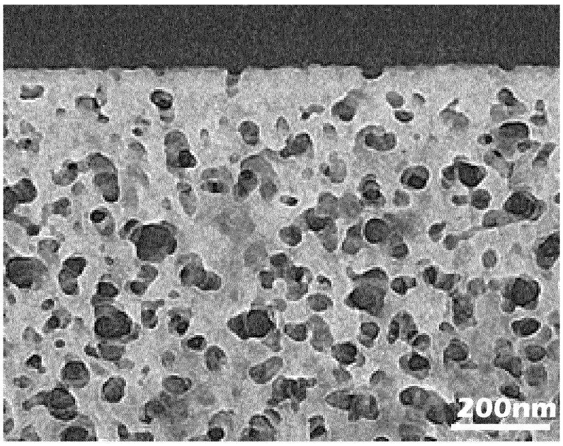
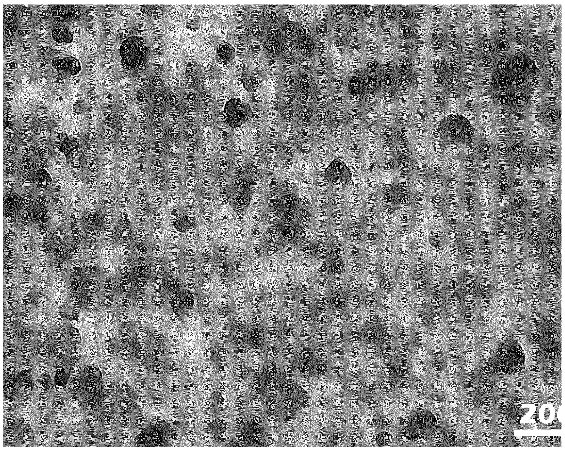


Figure 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/031124

A. CLASSIFICATION OF SUBJECT MATTER
D01F6/18(2006.01)i, *D01F9/22*(2006.01)i

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)
D01F1/00-6/96, 09/12-9/32

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011-1653 A (Toray Industries, Inc.), 06 January 2011 (06.01.2011), claims 1 to 2; paragraph [0025]; examples; table 1 (Family: none)	1-11
X Y A	JP 04-257313 A (Mitsubishi Rayon Co., Ltd.), 11 September 1992 (11.09.1992), claim 1; examples; tables 1, 4; paragraph [0032] (Family: none)	1-3,9,11 1,3,9,11 4-8,10
Y A	JP 2002-266172 A (Mitsubishi Rayon Co., Ltd.), 18 September 2002 (18.09.2002), paragraphs [0009], [0026]; examples; table 1 (Family: none)	1,3,9,11 2,4-8,10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 06 October 2017 (06.10.17)	Date of mailing of the international search report 24 October 2017 (24.10.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/031124

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	WO 2010/143680 A1 (Mitsubishi Rayon Co., Ltd.), 16 December 2010 (16.12.2010), paragraph [0029]; examples; tables 1 to 2 & US 2012/0088104 A1 paragraph [0042]; examples; tables 1 to 2 & EP 2441865 A1 & CA 2764661 A & CN 102459722 A & KR 10-2012-0023181 A & TW 201114960 A & CA 2820810 A & CA 2820976 A & ES 2534649 T	1,3,9,11 2,4-8,10
Y A	JP 2007-23476 A (Mitsubishi Rayon Co., Ltd.), 01 February 2007 (01.02.2007), paragraphs [0031], [0035] & JP 2004-183194 A	1,3,9,11 2,4-8,10
A	JP 9-268426 A (Kuraray Co., Ltd.), 14 October 1997 (14.10.1997), (Family: none)	1-11

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2010143680 A **[0007]**
- JP HEI274607 B **[0007]**
- JP 2010100970 A **[0007]**

Non-patent literature cited in the description

- Hansen Solubility Parameters A User's Handbook. CRC Press, 2007 **[0029]**