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(54) Titre : FIL EN ACRYLONITRILE EXPANSE POUR UNE FIBRE DE CARBONE, FAISCEAU DE FIBRES DE PRECURSEUR, FAISCEAU DE FIBRES RESISTANT A LA FLAMME, FAISCEAU DE FIBRES DE CARBONE ET PROCEDES DE PRODUCTION DE CE FIL

(54) Title: ACRYLONITRILE SWOLLEN FIBER FOR CARBON FIBER, PRECURSOR FIBER BUNDLE, STABILIZED FIBER BUNDLE, CARBON FIBER BUNDLE AND PRODUCTION METHODS THEREOF

(57) Abrégé/Abstract:
Provided is a carbon fiber bundle for obtaining a fiber-reinforced plastic having high mechanical characteristics. An acrylonitrile swollen fiber for a carbon fiber having openings of 10 nm or more in width in the circumference direction of the swollen fiber at a ratio in the range of 0.3 openings/μm^2 or more and 2 openings/μm^2 or less on the surface of the swollen fiber, and the swollen fiber is not treated with a finishing oil agent. A precursor fiber obtained by treating the swollen fiber with a silicone-based finishing oil agent has a silicon content of 1700 ppm or more and 5000 ppm or less, and the silicon content is 50 ppm or more and 300 ppm or less after the finishing oil agent is washed away with methyl ethyl ketone by using a Soxhlet extraction apparatus for 8 hours. The fiber is preferably an acrylonitrile copolymer containing acrylonitrile in an amount of 96.0 mass % or more and 99.7 mass % or less and an unsaturated hydrocarbon having at least one carboxyl group or ester group in an amount of 0.3 mass % or more and 4.0 mass % or less.

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Abstract

Provided is a carbon fiber bundle for obtaining a fiber-reinforced plastic having high mechanical characteristics. An acrylonitrile swollen fiber for a carbon fiber having openings of 10 nm or more in width in the circumference direction of the swollen fiber at a ratio in the range of 0.3 openings/μm^2 or more and 2 openings/μm^2 or less on the surface of the swollen fiber, and the swollen fiber is not treated with a finishing oil agent. A precursor fiber obtained by treating the swollen fiber with a silicone-based finishing oil agent has a silicon content of 1700 ppm or more and 5000 ppm or less, and the silicon content is 50 ppm or more and 300 ppm or less after the finishing oil agent is washed away with methyl ethyl ketone by using a Soxhlet extraction apparatus for 8 hours. The fiber is preferably an acrylonitrile copolymer containing acrylonitrile in an amount of 96.0 mass % or more and 99.7 mass % or less and an unsaturated hydrocarbon having at least one carboxyl group or ester group in an amount of 0.3 mass % or more and 4.0 mass % or less.

Description

Title of Invention:

ACRYLONITRILE SWOLLEN FIBER FOR CARBON FIBER, PRECURSOR FIBER BUNDLE, STABILIZED FIBER BUNDLE, CARBON FIBER BUNDLE AND PRODUCTION METHODS THEREOF

Technical Field

[0001]

The present invention relates to a carbon fiber bundle that has excellent mechanical characteristics and that can be used to obtain a high-quality and high-performance fiber-reinforced plastic particularly for airplane use, industrial use, etc., and the invention relates to a swollen fiber, a precursor fiber bundle and a stabilized fiber bundle for use in producing the same.

Background Art

[0002]

In order to improve the mechanical characteristics of resin-base molded products, a resin has been commonly used in combination with a fiber serving as a reinforcement material. In particular, a composite molding material formed of a carbon fiber that is excellent in specific strength and specific elasticity in combination with a high-performance resin develops extremely excellent mechanical characteristics. Because of this, such a molding material has been willingly used as a constructional material for airplanes, high speed moving bodies, etc. Furthermore, there is a demand for developing a material that is stronger and that has higher rigidity as well as having excellent specific strength and specific rigidity. Given these circumstances, the desire is for further

improvement of the performance of carbon fiber, such as improved strength and elastic modulus.

[0003]

What is required in order to produce such a high performance carbon fiber includes obtaining an acrylonitrile precursor fiber bundle for a carbon fiber having excellent strength and carbonizing the precursor fiber bundle under optimal conditions. In particular, research has been conducted for densifying a precursor fiber bundle structure, completely removing points from which defects start, and finding carbonizing conditions under which defects are rarely formed. For example, Patent Literature 1 proposes a method of drawing a coagulated fiber that still contains a solvent in a solvent-containing drawing bath, thereby improving uniformity in structure and orientation, in order to obtain a precursor fiber bundle by a dry-wet spinning method. Drawing a coagulated fiber in a bath containing a solvent is a method commonly known as a solvent drawing technique that enables a stable drawing process by using solvent plasticization. Accordingly, this method is considered as an extremely excellent technique for obtaining a fiber that has high uniformity in structure and orientation. However, if a fiber bundle that is in a swollen state due to the presence of a solvent is drawn, the solvent within a filament is rapidly squeezed out from the filament simultaneously upon drawing. The resultant structure of the filament tends to be less dense and thus a desired filament that has a dense structure cannot be obtained. As a result, it has been difficult to obtain a carbon fiber bundle having high strength.

[0004]

Furthermore, Patent Literature 2, which pays attention to fine pores distributed in a coagulated fiber, proposes a technique for obtaining a precursor fiber in which excellent strength is developed by dry

densification of a coagulated fiber that has a high-dense structure. The fine pore distribution, which is obtained by a mercury press-in method, reflects the bulk state from the surface layer to the interior of the filament. This is an extremely excellent method for evaluating the overall density of a fiber structure. From the precursor fiber bundle that has at least a certain level density as a whole, a very strong carbon fiber can be obtained in which defect formation is prevented. However, observation of fractures in the carbon fiber shows that fractures have originated from near the surface layer at an extremely high ratio. This means that a defect is present near the surface layer. In other words, this technique is insufficient for manufacturing a precursor fiber bundle that is excellent in density near the surface layer.

[0005]

Patent Literature 3 proposes a method for manufacturing an acrylonitrile-based precursor fiber bundle that is not only high in whole density but also that is extremely high in surface density. Furthermore, Patent Literature 4 proposes, taking into consideration that a finishing oil agent enters the surface-layer portion of a fiber and inhibits densification, a technique for preventing permeation of a finishing oil agent by focusing on microscopic voids of the surface-layer portion. However, a technique for preventing entry of a finishing oil agent and a technique for preventing defect formation are both difficult to put into practical use since very complicated steps are required. Therefore, in the techniques discussed above, the effect of stably preventing the entry of a finishing oil agent into the surface layer portion is insufficient and the effect of reinforcing a carbon fiber is still far from a sufficient level.

Citation List

Patent Literature

[0006]

Patent Literature 1: JP05-5224A

Patent Literature 2: JP04-91230A

Patent Literature 3: JP06-15722B

Patent Literature 4: JP11-124744A

Summary of Invention

Technical Problem

[0007]

An object of the present invention is to provide a carbon fiber bundle for obtaining fiber-reinforced plastic that has high mechanical characteristics.

Solution to Problem

[0008]

The present inventors conducted research with the view to attaining the aforementioned object. They clarified proper forms and properties of an acrylonitrile swollen fiber for a carbon fiber and precursor fiber bundle; at the same time, they found that a swollen fiber having a dense inner structure and capable of preventing permeation of a finishing oil agent near a surface layer can be obtained by optimizing coagulation conditions and drawing conditions for spun fiber.

[0009]

The aforementioned object can be attained by the following inventions.

A first invention is directed to an acrylonitrile swollen fiber for a carbon fiber having openings of 10 nm or more in width in the circumference direction of the swollen fiber at a ratio in the range of 0.3 openings/μm^2 or more and 2 openings/μm^2 or less on the surface of the

swollen fiber, in which the swollen fiber is not treated with a finishing oil agent.

[0010]

A second invention is directed to a method of producing a swollen fiber, including

[1] a step of preparing a dope at a temperature of 50°C or more and 70°C or less by dissolving an acrylonitrile-based copolymer, which is obtained by copolymerizing acrylonitrile in an amount of 96.0 mass % or more and 99.7 mass % or less and an unsaturated hydrocarbon having at least one carboxyl group or ester group in an amount of 0.3 mass % or more and 4.0 mass % or less, as essential components, in an organic solvent in a concentration in the range of 20 mass % or more and 25 mass % or less,

[2] a step of obtaining a coagulated fiber bundle containing the organic solvent by ejecting the dope from ejection holes into the air by use of a dry-wet spinning method, followed by coagulating in a coagulation bath constituted of an aqueous solution containing an organic solvent in a concentration of 78.0 mass % or more and 82.0 mass % or less, at a temperature of -5°C or more and 20°C or less,

[3] a step of drawing the coagulated fiber bundle in the air at a ratio in the range of 1.0 time or more and 1.25 times or less, followed by further drawing in a warm aqueous solution containing an organic solvent, wherein a total draw ratio in both drawing processes is 2.6 times or more and 4.0 times or less, and

[4] a step of subsequently removing the solvent with warm water and further drawing in hot water at a ratio of 0.98 times or more and 2.0 times or less.

[0011]

A third invention is directed to a precursor fiber bundle for a carbon

fiber formed of an acrylonitrile copolymer, which is obtained by copolymerizing acrylonitrile in an amount of 96.0 mass % or more and 99.7 mass % or less and an unsaturated hydrocarbon having at least one carboxyl group or ester group in an amount of 0.3 mass % or more and 4.0 mass % or less, as essential components, and having a silicon content of 1700 ppm or more and 5000 ppm or less when the fiber bundle is treated with a finishing oil agent containing silicone compounds as main components, wherein the silicon content is 50 ppm or more and 300 ppm or less after the finishing oil agent is washed away with methyl ethyl ketone by using a Soxhlet extraction apparatus for 8 hours.

[0012]

A fourth invention is directed to a method of producing a precursor fiber bundle for a carbon fiber including applying a finishing oil agent containing silicone compounds as main components to a bundle of the swollen fiber in an amount of 0.8 mass % or more and 1.6 mass % or less based on 100 mass % of the swollen fiber, followed by drying and then drawing by a heat drawing method or by a steam drawing method at a ratio in the range of 1.8 times or more and 6.0 times or less.

[0013]

A fifth invention is directed to a method of producing a stabilized fiber bundles including feeding the precursor fiber bundle to a hot-air circulation type oven for stabilization at a temperature of 220 to 260°C for 30 minutes or more and 100 minutes or less, thereby applying heat treatment at an extension rate of 0% or more and 10% or less under an oxidizing atmosphere, the method satisfying the following 4 conditions:

(1) intensity ratio (B/A) of peak A (2θ = 25°) and peak B (2θ = 17°) in the equatorial-line direction, which is determined by wide angle x-ray diffraction measurement of the fiber bundle, is 1.3 or more,

(2) orientation degree of peak B is 80% or more,

(3) orientation degree of peak A is 79% or more and

(4) density is 1.335 g/cm^3 or more and 1.360 g/cm^3 or less.

[0014]

A sixth invention is directed to a carbon fiber bundle, wherein the strength of a strand impregnated with a resin is 6000 MPa or more, the strand elastic modulus measured by an ASTM method is 250 to 380 GPa, the ratio of the major axis and the minor axis (major axis/minor axis) of a cross section of a single fiber perpendicular to the fiber-axis direction is 1.00 to 1.01, the diameter of a single fiber is 4.0 μm to 6.0 μm, and the number of voids having a diameter of 2 nm or more and 15 nm or less present in the cross section of a single fiber perpendicular to the fiber-axis direction is 1 or more and 100 or less.

[0015]

A seventh invention is directed to a method of producing a carbon fiber bundle including treating the precursor fiber bundle with heat under an oxidizing atmosphere to obtain a stabilized fiber bundle having a density of 1.335 g/cm^3 or more and 1.355 g/cm^3 or less; then performing heating in a first carbonization furnace having a temperature gradient of 300°C or more and 700°C or less under an inert atmosphere while extending the extension rate to a rate of 2% or more and 7% or less for 1.0 minute or more to 3.0 minutes or less; and subsequently performing a heat treatment in at least one carbonization furnace having a temperature gradient from 1000°C to a desired temperature under an inert atmosphere while extending the extension rate to a rate of -6.0% or more and 2.0% or less for 1.0 minute or more and 5.0 minutes or less.

Advantageous Effects of Invention

[0016]

The swollen fiber of the present invention is capable of preventing

silicone oil serving as main components of a finishing oil agent from permeating into a surface layer portion of a precursor fiber. The carbon fiber bundle, which is obtained by subjecting the precursor fiber bundle to stabilization and carbonization treatment, has excellent mechanical performance and can provide a fiber-reinforced plastic having high mechanical characteristics.

Description of Embodiments

[0017]

In the present invention, the coagulated fiber refers to a fiber that is undergoing processing and that is removed from a coagulant and not yet subjected to drawing treatment. The swollen fiber refers to a fiber that is undergoing processing and that is obtained by applying drawing treatment and washing treatment to a coagulated fiber, in other words, a fiber that is undergoing processing before finishing oil agent attachment and dry treatment are applied.

[0018]

[Swollen fiber]

The acrylonitrile swollen fiber for a carbon fiber (hereinafter appropriately referred to as "swollen fiber") of the present invention has openings of 10 nm or more in width in the circumferential direction of a fiber within the ratio in the range of 0.3 openings/μm^2 or more and 2 openings/μm^2 or less on the surface of a single fiber before oil finishing treatment is applied. The swollen fiber, to which a finishing oil agent containing silicone compounds is applied, is dried and is then subjected to a drawing step to provide a precursor fiber bundle. Since the swollen fiber has such a surface, permeation of the oil components into the swollen-fiber surface layer portion can be significantly prevented.

[0019]

As the polymer constituting a swollen fiber, an acrylonitrile-based copolymer is preferred, which contains an acrylonitrile unit (96.0 mass % or more and 99.7 mass % or less) and an unsaturated hydrocarbon unit having at least one carboxyl group or ester group (0.3 mass % or more and 4.0 mass % or less) as essential components. Since the content of acrylonitrile unit is set to be 96.0 mass % or more and 99.7 mass % or less, structural irregularity of a ladder polymer formed by a stabilization reaction can be reduced. Consequently, during the following high-temperature treatment, a decomposition reaction can be prevented to provide a dense carbon fiber having few defects, which lower strength. Furthermore, the unsaturated hydrocarbon component having a carboxyl group or an ester group is known to serve as a starting point of a stabilization reaction in a stabilization step. If the content thereof is set to be 0.3 mass % or more and 4.0 mass % or less, stabilized fiber suitable for obtaining a carbon fiber at high yield, which is formed of a Graphene laminate structure having few structural irregularity and defects, can be obtained.

[0020]

The swollen fiber can be evaluated for whether it has a surface layer portion capable of preventing permeation of a finishing oil agent component by applying a predetermined amount of a finishing oil agent containing predetermined silicone-based compounds, applying dry densification to it, extracting and washing away the finishing oil agent with methyl ethyl ketone for 8 hours, and quantifying the remaining silicone-based compounds.

[0021]

[Evaluation of permeability of swollen fiber with finishing oil agent]

The permeability of a swollen fiber with a finishing oil agent can be evaluated as follows:

First, the following (1) amino-modified silicone oil and (2) an emulsifier are blended and subjected to a phase-transfer emulsification process to prepare an aqueous dispersion (a water-based finishing oil agent for fibers). The water based finishing oil agent for fibers is applied onto a swollen fiber.

(1) Amino-modified silicone; KF-865 (manufactured by Shin-Etsu Chemical Co., Ltd., mono amino modified side-chain type, kinematic viscosity: 110 cSt (25°C), amino equivalent mass: 5,000 g/mol): 85 mass %,

(2) Emulsifier; NIKKOL BL-9EX (manufactured by Nikko Chemicals Co., Ltd., POE (9) lauryl ether): 15 mass %.

[0022]

Subsequently, a dry process is performed by a dry roll to completely vaporize water and the swollen fiber is drawn twofold between heated rolls. In this manner, a fiber bundle containing silicon in an amount of 1700 ppm or more and 5000 ppm or less determined by a fluorescent X-ray apparatus is obtained. Then, the fiber bundle, from which the finishing oil agent is extracted and washed with methyl ethyl ketone in a Soxhlet extraction apparatus for 8 hours, is measured for silicon content by the fluorescent X-ray apparatus.

For the swollen fiber of the present invention, the silicon content (residual amount), after finishing oil agent is extracted and washed, is preferably 50 ppm or more and 300 ppm or less. This value is more preferably 50 ppm or more and 200 ppm or less.

[0023]

The silicon content of more than 300 ppm in the fiber bundle, after finishing oil agent is extracted and washed, means that the surface layer portion, which prevents permeation of a finishing oil agent component into the surface layer portion, does not have sufficient density. The resultant

carbon fiber obtained through a carbonization step will have many voids in the surface layer portion. As a result, a desired high-strength carbon fiber cannot be obtained. In contrast, the silicon content of less than 50 ppm means that the amount of finishing oil agent that permeates into the surface layer portion of a swollen fiber is extremely low. This is considered because a highly density skin layer is formed in the surface layer portion of a fiber in a coagulation bath.

[0024]

Furthermore, the swollen fiber of the present invention more preferably has a swelling degree of 80 mass % or less, which is measured in accordance with the method, i. e., [2. Method of measuring swelling degree of swollen fiber], which will be described later. The swelling degree of more than 80 mass % means that the density of the inner-layer structure of a swollen fiber slightly decreases. In this case, even if formation of defects is successfully prevented in the surface layer portion, the possibility of forming defects in an inner layer portion is high. As a result, a carbon fiber having high mechanical performance cannot be obtained. A further preferable swelling degree is 75 mass % or less.

[0025]

Furthermore, the density of swollen fiber can also be evaluated by measurement of a fine pore distribution within a fiber. The average fine pore size of the swollen fiber of the present invention is 55 nm or less and the total fine pore volume is preferably 0.55 ml/g or less. The average fine pore size is more preferably 50 nm or less and further preferably 45 nm or less. Furthermore, the total fine pore volume is more preferably 0.50 ml/g or less and further preferably 0.45 ml/g or less. Such a swollen fiber has no large voids within the fiber, and further, the ratio occupied by voids is low. Thus, the fiber is dense. If a dense skin layer is formed in a fiber surface in a coagulation bath, the size and volume of fine pores

within the fiber tend to increase. To obtain a desired high strength carbon fiber, it is preferable to satisfy the both conditions in which the permeation of a finishing oil agent is prevented by densifying the surface layer portion of a swollen fiber, as mentioned above, and in which the swollen fiber has a dense structure that has few voids within the fiber. Note that, the fine pore distribution of a swollen fiber is measured in accordance with the method, i. e., [4. Method of measuring fine pore distribution of swollen fiber], which will be described later.

[0026]

[Method of producing swollen fiber]

The swollen fiber of the present invention can be produced by subjecting a dope containing an acrylonitrile-based copolymer and an organic solvent to wet spinning or dry-wet spinning.

Examples of the acrylonitrile-based copolymer include an acrylonitrile-based copolymer obtained by copolymerizing acrylonitrile and an unsaturated hydrocarbon having at least one carboxyl group or ester group as essential components. Examples of the unsaturated hydrocarbon having at least one carboxyl group or ester group include acrylic acid, methacrylic acid, itaconic acid, methyl acrylate, methyl methacrylate and ethyl acrylate. An acrylonitrile copolymer obtained by copolymerizing any one of these or two or more compounds of these (0.3 mass % or more and 4.0 mass % or less) and acrylonitrile (96.0 mass % or more and 99.7 mass % or less) is preferably used. The acrylonitrile content is more preferably 98 mass % or more.

[0027]

An unsaturated hydrocarbon having a carboxyl group or an ester group is known to serve as a starting point of a stabilization reaction in a stabilization step. If the content thereof is excessively low, the stabilization reaction does not sufficiently proceed, interfering with

formation of the structure of a stabilized fiber. In contrast, if the content is excessively large, a reaction rapidly occurs due to the presence of many reaction starting points. As a result, a coarse structural form is formed and a carbon fiber having high performance cannot be obtained. If the content is set to be 0.3 mass % or more and 4.0 mass % or less, the stabilization reaction starting point and the rate of the reaction are well balanced and a dense structure results. In addition, formation of a structural irregularity, which will become a defect in a carbonization step, can be prevented. Furthermore, a stabilization reaction can be caused in a relatively low temperature range since the reaction system has moderate reactivity. From both economic and safety aspects, stabilization can be carried out. Accordingly, a stabilized fiber suitable for obtaining a carbon fiber formed of a Graphene laminate structure having few structural irregularities and defects at high yield can be obtained.

[0028]

As the third component, an acryl amide derivative such as acrylamide, methacrylamide, N-methylol acrylamide, N,N-dimethyl acrylamide, vinyl acetate, etc. may be used. As an appropriate method for copolymerizing a monomer mixture, any polymerization method may be used, including, for example, redox polymerization performed in an aqueous solution, suspension polymerization performed in non-homogeneous system and emulsion polymerization using a dispersant. Difference between the polymerization methods does not limit the present invention.

[0029]

In the spinning step, first, an acrylonitrile-based copolymer is dissolved in an organic solvent in a concentration of 20 to 25 mass % to prepare a dope having a temperature of 50 to 70°C. The solid-substance

concentration of the dope is preferably 20 mass % or more and more preferably 21 mass % or more. If the solid-substance concentration is set to be 20% or more, the amount of solvent migrating from the inside of a filament during a coagulation process can be reduced to obtain a coagulated fiber having the requisite density. In contrast, if the solid-substance concentration is set to be 25 mass % or less, a dope having the appropriate viscosity can be prepared, with the result that the dope can be stably ejected from a nozzle, rendering production easier. In short, if the solid-substance concentration is set to be 20 to 25 mass %, a coagulated fiber having a highly dense and uniform structure can be stably produced.

[0030]

Furthermore, if the temperature of a dope is set to be 50°C or more, the dope having the appropriate viscosity can be obtained without reducing the solid-substance concentration. Furthermore, if the temperature of a dope is set to be 70°C or less, the difference in temperature between the dope and the coagulant can be reduced. More specifically, if the temperature of a dope is 50 to 70°C, a coagulated fiber having a highly dense and uniform structure can be stably produced.

[0031]

The organic solvent is not particularly limited; however, dimethylformamide, dimethylacetamide or dimethylsulfoxide is more preferably used. More preferably, dimethylformamide which has excellent solubility for an acrylonitrile-based copolymer is used.

[0032]

The spinning method may be either wet spinning or dry-wet spinning. More preferably, dry-wet spinning is employed. This is because it is easy to form a dense coagulated fiber and, in particular, because the density of the surface layer portion can be enhanced. In dry-wet spinning, the dope prepared is spun from a spinneret having numerous nozzle holes arranged

therein into the air and then ejected in a coagulant filled with a solution mixture of an organic solvent and water and controlled in temperature to coagulate. The coagulated fiber is removed. The coagulant used herein preferably has a temperature of -5 to 20°C and a concentration of an organic solvent of 78 to 82 mass %. This is because a dense coagulated fiber can be easily formed within the range and, in particular, because the density of the surface layer portion can be enhanced. A more preferable temperature range of the aqueous solution is -5°C to 10°C and a more preferable concentration range of the organic solvent is 78.5 mass % or more and 81.0 mass % or less. If the organic solvent concentration of the coagulant is set to be 81.0 mass % or less, the density of the surface layer portion can be maintained and permeation of a finishing oil agent into a fiber surface layer portion can be prevented. Furthermore, if the organic solvent concentration is set to be 78.5 mass % or more, rapid coagulation of the surface layer during a coagulation process can be prevented, with the result that formation of a skin layer can be prevented. Furthermore, coagulation relatively slowly proceeds and thus an inner density does not decrease. More specifically, if the organic solvent concentration of the coagulant is set to be 78.5 to 81.0 mass %, a coagulated fiber that is dense not only in the surface layer portion but also in the inner portion of a fiber can be obtained.

[0033]

The coagulated fiber is subjected to drawing and washing treatment. The order of the drawing and washing treatment is not particularly limited. Drawing may be applied, followed by washing, and drawing and washing may be simultaneously performed. Any washing method may be employed as long as a solvent can be removed. In a particularly preferable drawing and washing treatment for a coagulated fiber, drawing is performed in a pre-drawing tank containing a liquid that has a lower

solvent concentration and higher temperature than a coagulant. Owing to this, a coagulated fiber having a uniform fibril structure can be formed.

[0034]

Conventionally, drawing a coagulated fiber in a bath containing a solvent has been generally known as a solvent drawing technique, which enables stable drawing treatment due to solvent plasticization, with the result that a fiber having high uniformity in structure as well as in orientation can be obtained. However, if a fiber bundle containing a solvent in a swollen state is subjected to drawing, as is, sufficient formation of a fibril structure and sufficient orientation of the structure by drawing cannot be obtained. Furthermore, since a finishing oil agent is also rapidly squeezed out from the inside of the filament, the resultant filament tends to have a non-dense structure and thus a swollen fiber that has a desired dense structure cannot be obtained. In the present invention, the temperature and concentration of a dope and a coagulant are optimally set. Based on this, if solvent drawing treatment is performed by optimally combining the conditions for a solvent drawing tank with draw ratio, a dense fibril structure can be formed.

[0035]

A coagulated fiber bundle containing an organic solvent is first drawn in the air, subsequently drawn in a drawing tank containing a warm aqueous solution that contains an organic solvent. The temperature of the warm aqueous solution preferably ranges from 40°C or more to 80°C or less. If the temperature is set to be 40°C or more, a good drawing property can be ensured, rendering formation of a uniform fibril structure easier. Furthermore, if the temperature is set to be 80°C or less, removal of the solvent from the surface of a fiber proceeds moderately without causing an excessive plasticizing action. Uniform drawing results. As a result, the quality of swollen fiber is improved. A more preferable

temperature is 55°C or more and 75°C or less.

Furthermore, concentration of the organic solvent in the warm aqueous solution that contains an organic solvent is preferably 30 mass % or more and 60 mass % or less. In the range of concentration, stable drawing treatment can be performed and a dense and uniform fibril structure can be formed in the inside and the surface layer. A more preferable concentration is 40 mass % or more and 50 mass % or less.

[0036]

In a preferable drawing method of a coagulated fiber, the draw ratio in the air is set to be 1.0 time or more and 1.25 times or less, and the sum of draw ratios in the air and in the warm aqueous solution is set to be 2.6 times or more and 4.0 times or less. The coagulated fiber has a swollen fibril structure containing a large amount of solvent. If the coagulated fiber formed of such a structure is drawn at a draw ratio of 1.0 time or more and 1.25 times or less in the air, formation of a non-dense fibril structure can be avoided. Furthermore, if the draw ratio is set to be 1.0 time or more, non-uniform shrinkage can be prevented.

[0037]

Furthermore, if the sum of draw ratios in the air and in a warm aqueous solution is set to be 2.6 times or more, sufficient drawing can be applied and a desired fibril structure having orientation in the fiber-axis direction can be formed. Furthermore, if the sum of draw ratios is set to be 4.0 times or less, a precursor fiber bundle having a dense structural form can be obtained without breakage of the fibril structure itself. In short, a dense fibril structure having orientation in the fiber-axis direction can be formed in the range of 2.6 times or more and 4.0 times or less. A more preferable sum of draw ratios is 2.7 times or more and 3.5 times or less.

[0038]

Furthermore, more preferably, drawing is performed in a warm aqueous solution containing an organic solvent at a draw ratio of 2.5 times or more. This is because drawing can be performed without collapse at the structure since the drawing in the warm aqueous solution that contains an organic solvent is performed at a relatively high temperature. Therefore, regarding the proportion of a draw ratio between the drawings in the air and in the warm aqueous solution that contains an organic solvent, the draw ratio in the warm aqueous solution that contains an organic solvent is preferably set to be higher. More preferably, the draw ratio in the air is 1.0 time or more and 1.15 times or less.

In this manner, a swollen fiber having a dense surface layer portion can be obtained. A more preferable dense swollen fiber is produced by using a coagulated fiber bundle containing an organic solvent with a swelling degree of 160 mass % or less in accordance with the aforementioned drawing method. This is because the coagulated fiber has a dense inner structure.

[0039]

After drawing treatment, the fiber bundle is washed with warm water of 50°C or more and 95°C or less to remove the organic solvent. Furthermore, after washing, if a fiber bundle that is in a swollen state and that lacks a solvent is drawn in hot water, the orientation of the fiber can be further enhanced. Alternatively, if relaxing treatment is slightly performed, distortion due to drawing can be removed. Preferably, drawing is performed at a ratio of 0.98 times or more and 2.0 times or less in hot water at a temperature of 70 to 95°C. Drawing performed at a draw ratio of 0.98 times or more and less than 1.0 time is a relaxation treatment. Removing distortion, which is produced by drawing in the previous step performed at a high draw ratio, from a fiber bundle is effective for stable drawing in the later drawing step. If drawing is

performed in the range of a draw ratio of 1.0 time or more and 2.0 times or less, the orientation degree of the fibril structure can be improved and the density of the surface layer can be increased. More preferably, drawing is performed at a ratio of 0.99 times or more and 1.5 times or less.

Swollen fiber can be obtained by applying drawing treatment and washing treatment to a coagulated fiber in this manner.

[0040]

[Heat drawing]

A predetermined amount of finishing oil agent is applied to a swollen fiber and subjected to dry densification. The method for dry densification is not particularly limited, and drying and densification are performed in accordance with a known dry method. A method of passing a swollen fiber through a plurality of heated rolls is preferably used. After dry densification, the fiber bundle is drawn in a pressurized steam of 130 to 200°C, in a dry heat medium of 100 to 200°C, between heated rolls of 150 to 220°C or on a heated plate of 150 to 220°C to further improve orientation and to perform densification. Thereafter, the bundle is wound to obtain a precursor fiber bundle.

[0041]

[Precursor fiber bundle]

A precursor fiber bundle for a carbon fiber (hereinafter appropriately referred to as a "precursor fiber bundle") of the present invention is formed of an acrylonitrile copolymer obtained by copolymerizing acrylonitrile (96.0 mass % or more and 99.7 mass % or less) and an unsaturated hydrocarbon having at least one carboxyl group or ester group (0.3 mass % or more and 4.0 mass % or less) as essential components. The precursor fiber bundle has a silicon content of 1700 ppm or more and 5000 ppm or less after being treated with a finishing oil agent containing silicone-based compounds as main components and a

silicon content of 50 ppm or more and 300 ppm or less after the finishing oil agent is washed away with methyl ethyl ketone by using a Soxhlet extraction apparatus for 8 hours. The silicon content is measured by a fluorescent X-ray apparatus. Furthermore, the silicon content after the finishing oil agent is washed away is a measured value based on evaluation in the above section [Evaluation of permeability of swollen fiber with finishing oil agent] performed through the steps of applying a finishing oil agent and washing finishing oil agent.

[0042]

After treatment with a finishing oil agent, if the silicon content of a precursor fiber bundle is 1700 ppm to 5000 ppm or less, fusion between filaments in a stabilization step does not occur; however, oxygen diffusion into a filament is inhibited by the presence of an excessive amount of silicone compounds in the surface layer. Consequently, there are no portions at which a stabilization reaction is not sufficiently performed and the occurrence of fiber breakage can be prevented in a step of carbonization treatment performed at a higher temperature. As a result, it is ensured that the fiber bundle stably passes through a manufacturing process.

[0043]

The precursor fiber bundle of the present invention has a silicon content of 300 ppm or less after a finishing oil agent is extracted and washed away. A silicon content of more than 300 ppm means that oil of silicone-based compounds permeates into a surface layer portion and the amount of oil that is present therein increases. As a result, the silicone oil that is present in the surface layer portion remains without being scattered in a stabilization step and in a first-half carbonization step (800°C or less) of a carbonization step, and is scattered in a second-half carbonization step (more than 800°C). As a result, many voids are

formed in the surface layer portion of the final carbon fiber. Accordingly, a desired high-strength carbon fiber cannot be obtained. In contrast, the silicon content of the fiber bundle being 300 ppm or less after a finishing oil agent is extracted and washed away means that the silicon compounds applied to a precursor fiber permeates into the surface layer portion and is present near the outermost surface in the surface layer portion of the precursor fiber. Thus, because the amount of the silicon compounds that are difficult to extract is low, the silicon compounds are present in the outermost surface layer portion. If such a state is present, silicone-based compounds can be scattered from the outermost surface layer portion in a stabilization step and in a carbonization step of a carbonization step, without forming defects. More preferable silicon content after a finishing oil agent is extracted and washed away is 200 ppm or less by mass.

[0044]

In the precursor fiber bundle, preferably the fineness of a single fiber is 0.5 dtex or more and 1.0 dtex or less; a ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single fiber is 1.00 or more and 1.01 or less; an uneven surface structure extending in the fiber-axis direction of a single fiber is not present; the difference in height (Rp-v) between a highest portion and a lowest portion is 30 nm or more and 100 nm or less; and a center-line average roughness (Ra) is 3 nm or more and 10 nm or less. If an (Rp-v) value is 30 nm or more or an (Ra) value is 3 nm or more, the smoothness of the surface of a precursor fiber filament is not excessive. This means that small breakage of a surface-layer fibril does not occur because of the low drawing property in a spinning step due to the skin layer formed in a coagulation step. Thus, formation of micro defects can be avoided. In addition, non-uniform stabilization can be avoided, which is caused by inhibition of oxygen

diffusion into an inner portion of a filament in a stabilization step due to excessive converging of a fiber bundle, which is an assembly of filaments. In contrast, if the (Rp-v) value is set to be 100 nm or less or if the (Ra) value is set to be 10 nm or less, the density of a structure near a surface layer can be conceivably set to a sufficient level. In short, if a filament has a surface that satisfies an (Rp-v) value of 30 nm or more and 100 nm or less and an (Ra) value of 3 nm or more and 10 nm or less, the structure of the filament will have a sufficient density near the surface layer and sufficient drawing property. The probability of defect formation near a surface layer from a spinning step to a carbonization step can be reduced. As a result, a high-strength carbon fiber bundle can be obtained.

[0045]

The uneven surface structure extending in the fiber-axis direction herein refers to a wrinkle structure that has a length of 0.6 μm or more and that is present almost parallel to the fiber-axis direction. The acrylonitrile fiber bundle causes volume shrinkage usually due to coagulation and the following drawing treatment. As a result, a wrinkle structure that extends in the fiber-axis direction is formed on the surface. Formation of the wrinkle structure can be prevented by preventing formation of a rigid skin layer in a coagulation step, thereby realizing gradual volume shrinkage. Furthermore, it is known that formation of the wrinkle structure is significantly prevented by dry-wet spinning. Preferably, the precursor fiber bundle does not have such a wrinkle structure having a length of 0.6 μm or more.

[0046]

A fiber having a ratio of the major axis and the minor axis (major axis/minor axis) of a single-fiber cross-section of 1.00 to 1.01, is a single fiber having a complete circular or nearly complete circular cross-section and is excellent in structural uniformity near the fiber surface. A more

preferable ratio of the major axis and the minor axis (major axis/minor axis) is 1.00 to 1.005.

A fiber having a fineness of a single fiber within the range of 0.5 to 1.0 dtex has a small fiber diameter. Thus, the degree of structural non-uniformity developed in the cross-section direction in a carbonization step can be reduced. A more preferable range is 0.5 to 0.8 dtex.

[0047]

[Method of producing precursor fiber bundle]

A precursor fiber bundle containing silicon in the aforementioned predetermined amount can be produced by applying a finishing oil agent that contains silicone compounds as main components to the swollen fiber of the present invention and drying it, and then by applying a drawing treatment in accordance with hot drawing or steam drawing.

[0048]

The silicone compound that serves as the main component of the finishing oil agent is not particularly limited; however, taking into consideration interaction with an acrylonitrile-based copolymer, an amino-modified polydimethyl siloxane or an epoxy-modified polydimethyl siloxane is preferably used. In particular, since the swollen fiber of the present invention has a highly dense surface layer portion, taking into account the ease of coating the surface layer, and further, taking into account the difficulty of removing the finishing oil agent from the surface layer, an amino-modified polydimethyl siloxane is preferred.

Furthermore, in the case where methyl groups of a polydimethyl siloxane skeleton are partly substituted with phenyl groups, such a compound is excellent in view of the heat resistance characteristics of the compound. The most preferable amino-modified polydimethyl siloxane has a kinematic viscosity of 50 to 5,000 cSt at 25°C and an amino equivalent mass of 1,700 to 15,000 g/mol.

[0049]

The type of modification with an amino acid is not particularly limited; however, a mono amino modified side-chain type, a diamino modified side-chain type and a two-end modification type are preferred. Furthermore, a mixture of these or a mixture of a plurality of types can be used. If the kinematic viscosity at 25°C is 50 cSt or more, such a compound is non-volatile and has a sufficient molecular weight. In this case, scattering from a fiber can be prevented throughout the stabilization step and the finishing oil agent plays the role that is required in the process, with the result that a carbon fiber can be stably produced. Furthermore, if the kinematic viscosity at 25°C is set to be 5000 cSt or less, part of the finishing oil agent is transferred from a fiber bundle to a roll etc. in a stabilization step. If the finishing oil agent transferred is treated with heat for a relatively long time, the viscosity thereof increases and becomes sticky, with the result that part of a fiber bundle is wound around a roll. Such trouble frequently occurs. Furthermore, if an amino equivalent mass is set to be 1,700 g/mol or more, heat reactivity of silicone is prevented. As a result, the occurrence of problems, i.e., winding of part of a fiber bundle around a roll caused by a finishing oil agent transferred from the fiber bundle to a roll etc. can be avoided. If the amino equivalent mass is set to be 15,000 g/mol or less, due to sufficient affinity of a precursor fiber for silicone, scattering from a fiber can be prevented throughout the stabilization step. In short, if the kinematic viscosity of a finishing oil agent at 25°C is 50 to 5,000 cSt and if the amino equivalent mass falls within the range of 1,700 to 15,000 g/mol, a process from spinning to stabilization can be continuously and stably performed for a long time without any problem being caused by a finishing oil agent being transferred to a roll etc., such as winding of a fiber around the roll and abrupt scattering of the finishing oil agent in a stabilization

step.

[0050]

Examples of amino-modified polydimethyl siloxane of the mono amino modified side-chain type include KF-864, KF-865, KF-868, and KF-8003 (all are manufactured by Shin-Etsu Chemical Co., Ltd.). Examples of amino-modified polydimethyl siloxane of the diamino modified side-chain type include KF-859, KF-860, KF-869, and KF-8005 (all are manufactured by Shin-Etsu Chemical Co., Ltd.). Examples of amino-modified polydimethyl siloxane of the two-end modification type include Silaplane FM-3311, FM-3221, FM-3325 (all are manufactured by Chisso Corporation) and KF-8012 (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0051]

The finishing oil agent is constituted of compounds such as a surfactant for forming an aqueous emulsion, and a softening agent and a lubricant agent for imparting excellent processability. As the surfactant, a nonionic surfactant is mainly used. Pluronic type and EO/PO adduct of a higher alcohol are used. In particular, polyoxyethylene/polyoxypropylene block polymers, namely, NEWPOL PE-78, PE-108, and PE-128 (all are products by Sanyo Chemical Industries, Ltd.) are preferred.

[0052]

As the softening agent and lubricant agent, an ester compound and a urethane compound are used. The content of silicone compounds in a finishing oil agent is 30 mass % to 90 mass %. If the content is 30 mass % or more, fusion is sufficiently prevented in a stabilization step. Furthermore, if the content is 90 mass % or less, an emulsion of the finishing oil agent can be easily stabilized at a sufficient level and a precursor fiber can be stably produced. In short, if the content of

silicone-based compounds in a finishing oil agent is 30 mass % to 90 mass %, even in a precursor fiber having a dense surface, as in the present invention, fusion will be sufficiently prevented in a stabilization step, and stability in a finishing oil agent attachment step as well as a uniform application state can be realized. Therefore, performance of the resultant carbon fiber can be stably developed.

[0053]

The applied amount of a finishing oil agent containing silicone compounds as main components is 0.8 mass % to 1.6 mass %. After the finishing oil agent is applied, the fiber is subjected to dry densification. The dry densification is not particularly limited and dry densification can be performed in accordance with a known drying method. Preferably, a method of passing a fiber through a plurality of heated rolls is employed. If the applied amount of finishing oil agent is set to be 0.8 to 1.6 mass %, fusion of fibers that are caused by insufficient coating with the finishing oil agent and structural irregularity of a stabilized fiber that is caused by insufficient diffusion of oxygen due to excessive application of a finishing oil agent can be reduced, with the result that carbon fiber having high strength can be produced.

[0054]

The fiber bundle after the dry densification process is, if necessary, drawn in a pressurized steam at a temperature of 130 to 200°C, in a dry heat medium, between heated rolls or on a heated plate at a ratio of 1.8 to 6.0 times to further improve orientation and to perform densification. In this manner, a precursor fiber bundle is obtained. A more preferable draw ratio is 2.4 to 6.0 times and further preferably 2.6 to 6.0 times.

[0055]

[Method of producing a stabilized fiber bundle]

A precursor fiber bundle is fed to a hot-air circulation type oven for

stabilization at a temperature of 220 to 260°C for 30 minutes or more and 100 minutes or less to apply heat treatment under an oxidizing atmosphere at an extension rate of 0% or more and 10% or less. In this manner, a stabilized fiber bundle having a density of 1.335 g/cm^3 or more and 1.360 g/cm^3 or less can be obtained. The stabilization reaction includes a cyclization reaction with heat and an oxidation reaction with oxygen. It is important to balance the two reactions. To balance the two reactions, the amount of time for conducting stabilization is preferably 30 minutes or more to 100 minutes or less. If the reaction time is less than 30 minutes, a portion of a single fiber in which the oxidation reaction does not sufficiently proceed, is present within the single fiber, with the result that a large structural plaque is generated in the cross-section direction of the single fiber. As a result, the obtained carbon fiber has a non-uniform structure and fails to develop high mechanical performance. In contrast, if the reaction time exceeds 100 minutes, a larger amount of oxygen is present near the surface of a single fiber. Thereafter, in the following heat treatment performed at a high temperature, a reaction that consumes an excessive amount of oxygen occurs, which results in a defect. As a result, a carbon fiber having high strength cannot be obtained.

[0056]

A more preferable stabilization time is 40 minutes or more and 80 minutes or less. If the density of a stabilized fiber is less than 1.335 g/cm^3, stabilization will be insufficient. In the following heat treatment performed at a high temperature, a decomposition reaction occurs resulting in the formation of a defect. Because of this, a carbon fiber having high strength cannot be obtained. If the density of a stabilized fiber exceeds 1.360 g/cm^3, the oxygen content of the fiber increases. In the following heat treatment performed at a high temperature, a reaction

that consumes an excessive amount of oxygen occurs, resulting in the formation of a defect. Because of this, a carbon fiber having high strength cannot be obtained. A more preferable density range of a stabilized fiber is 1.340 g/cm^3 or more and 1.350 g/cm^3 or less.

[0057]

Appropriate extension of a fiber performed in an oven for stabilization is required in order to maintain and improve orientation of a fibril structure constituting the fiber. If the extension is less than 0%, the orientation of a fibril structure cannot be maintained; orientation along the fiber axis does not sufficiently develop during the formation of a carbon fiber structure; and excellent mechanical performance will not develop. In contrast, if the extension exceeds 10%, a fibril structure itself will be broken, with the result that formation of a carbon fiber structure will be impaired. In addition, since a fracture point becomes a defect, a carbon fiber having high strength cannot be obtained. A more preferable extension rate is 3% or more and 8% or less.

[0058]

In a preferable method of producing a stabilized fiber bundle, a precursor fiber bundle is treated with heat under the aforementioned oxidizing atmosphere to obtain a stabilized fiber bundle that satisfies an intensity ratio (B/A) of peak A (2θ = 25°) and peak B (2θ = 17°) in the equatorial-line direction when the fiber bundle is measured by wide-angle X-ray: 1.3 or more; an orientation degree of peak A: 79% or more; an orientation degree of peak B: 80% or more; and a density: 1.335 g/cm^3 or more and 1.360 g/cm^3 or less.

[0059]

The crystal structure derived from reflection by polyacrylonitrile (100) at peak B (2θ = 17°) is closely related to formation of the structure of a carbon fiber. If the orientation degree of a crystal and crystallinity

are once lowered during the process for producing a carbon fiber, it will be difficult to return to the original states, with the result that development of performance of the carbon fiber will tend to decrease. The (100) used herein indicates the orientation of a crystal. In particular, a stabilization step is a step in which the structure of a precursor fiber significantly changes and a graphite crystal group, which is a fundamental structure of a carbon fiber, is formed. The crystal structure derived from reflection by polyacrylonitrile (100) at peak B (2θ = 17°) is significantly changed by a stabilization step and the degree of changes significantly varies depending upon the set conditions of the stabilizing process. To obtain a stabilized fiber having a high orientation, an appropriate treatment must be applied. Furthermore, the orientation degree is closely related with crystallinity. More specifically, crystallinity is significantly reduced as the degree of orientation is reduced. Conversely to say, if a high orientation can be maintained, a high crystalline fiber can accordingly be obtained. For the reason, a stabilized fiber bundle preferably has a crystal structure that satisfies an intensity ratio (B/A) of 1.3 or more, a peak-A orientation degree of 79% or more and a peak-B orientation degree of 80% or more.

[0060]

The aforementioned stabilized fiber bundle can be relatively easily obtained by using a precursor fiber bundle of the present invention. Furthermore, in a step of treating a precursor fiber bundle with heat under an oxidizing atmosphere, stabilizing conditions are preferably set so as to perform extension treatment separately under at least three sets of conditions: an extension rate of 3.0% or more and 8.0% or less at a fiber density in the range of 1.200 g/cm^3 or more and 1.260 g/cm^3 or less; an extension rate at 0.0% or more and 3.0% or less at a fiber density in the range of 1.240 g/cm^3 or more and 1.310 g/cm^3 or less; and an extension rate of -1.0% or more and 2.0% or less at a fiber density in the range of

1.300 g/cm^3 or more and 1.360 g/cm^3 or less.

[0061]

[Carbon fiber]

Next, a stabilized fiber bundle is heat treated for 1.0 minute to 3.0 minutes in a first carbonization furnace having a temperature gradient of 300°C or more and 800°C or less under an inert gas atmosphere such as nitrogen while extending the extension rate to a rate of 2% or more to 7% or less. A preferable processing temperature is 300°C to 800°C and the stabilized fiber bundle is processed in linear temperature gradient conditions. In consideration of the temperature in the previous step of stabilization, the initiation temperature is preferably 300°C or more. If the highest temperature exceeds 800°C, the fiber becomes very fragile and will be barely transferred to the following step. A more suitable temperature range is 300 to 750°C. More preferable temperature range is 300 to 700°C.

[0062]

The temperature gradient is not particularly limited; however a linear gradient is preferably employed. If the extension rate is less than 2%, orientation of a fibril structure cannot be maintained and orientation along the fiber axis in formation of a carbon fiber structure will not be sufficient, with the result that excellent mechanical performance cannot develop. In contrast, if the extension rate exceeds 7%, the fibril structure itself will be broken, with the result that subsequent formation of the carbon fiber structure will be impaired. In addition, since a fracture point becomes a defect, a carbon fiber having high strength cannot be obtained. A more preferable extension rate is 3% or more and 5% or less. The preferable treatment time is 1.0 minute to 3.0 minutes. If the treatment time is less than 1.0 minute, the temperature will abruptly increase, and this will be accompanied by a severe decomposition reaction. As a result, a carbon

fiber having high strength cannot be obtained. If the treatment time exceeds 3.0 minutes, the effect of plasticization in the first half of the step will be produced, with the result that orientation degree of a crystal will tend to decrease. As a result, the mechanical performance of the resultant carbon fiber will be impaired. The more preferable treatment time is 1.2 to 2.5 minutes.

[0063]

Subsequently, heat treatment is performed under tension in a second carbonization furnace that is capable of setting a temperature gradient in the range of 1000 to 1600°C under an inert atmosphere such as nitrogen to obtain a carbon fiber. Furthermore, if necessary, heat treatment is additionally performed under an inert atmosphere under tension in a third carbonization furnace having a desired temperature gradient. Temperature is set depending upon the desired elastic modulus of the carbon fiber. To obtain a carbon fiber having high mechanical performance, the highest temperature of carbonization treatment is preferably low. Furthermore, since the elastic modulus can be increased by increasing the treatment time, the highest temperature can be lowered. Moreover, the temperature gradient can be set so as to increase slowly by increasing the treatment time. This is effective in preventing defect formation.

[0064]

The temperature of the second carbonization furnace varies depending upon the temperature condition in the first carbonization furnace; however, the temperature is satisfactorily 1000°C or more and preferably 1050°C or more. The temperature gradient is not particularly limited; however a linear gradient is preferably employed. The treatment time is preferably 1.0 minute to 5.0 minutes and more preferably 1.5 minutes to 4.2 minutes. In the heat treatment, the fiber bundle

significantly shrinks. Thus, it is important to perform the heat treatment under tension. The extension rate is preferably -6.0% to 2.0%. If the extension rate is less than -6.0%, the orientation of a crystal in the fiber-axis direction will be unsatisfactory and sufficient performance cannot be obtained. In contrast, if the extension rate exceeds 2.0%, the structure so far formed itself will be broken and many defects will be formed, with the result that the strength will be significantly reduced. More preferable extension rate falls within the range of -5.0% to 0.5%.

[0065]

The carbon fiber bundle thus obtained is subjected to surface oxidization treatment. Examples of the surface treatment method include known methods, i.e., oxidation treatments such as electrolytic oxidation, chemical oxidation and air oxidation. Any one of these methods may be employed. The electrolytic oxidation treatment that is used widely in industry is the most preferable method since surface oxidization treatment can be stably performed and the surface treatment state can be controlled by varying the amount of electricity. In this case, even if the amount of electricity is the same, the state of the surface varies significantly depending upon the electrolyte and the concentration thereof that is employed; however, oxidation treatment is preferably performed in an aqueous alkaline solution that has a pH of more than 7 with a carbon fiber as an anode while supplying an electric quantity of 10 to 200 coulomb/g. Examples of electrolyte that is preferably used include ammonium carbonate, ammonium bicarbonate, calcium hydroxide, sodium hydroxide and potassium hydroxide.

[0066]

Next, the carbon fiber bundle is subjected to sizing treatment. The sizing agent is dissolved in an organic solvent or dispersed in water with the help of an emulsifier to prepare an emulsion. The above preparation

is applied to a carbon fiber bundle in accordance with a roller dip method, a roller contact method, etc. Subsequently, the carbon fiber bundle is dried. In this manner, sizing treatment can be performed. Note that the applied amount of the sizing agent that is applied to the surface of a carbon fiber can be controlled by controlling the concentration of the sizing agent solution and the amount of the sizing agent that is squeezed. Furthermore, drying can be performed by use of e.g., hot air, a hot plate, a heated roller and various infrared heaters. Subsequently, the sizing agent is applied and dried, and then, the carbon fiber bundle is wound onto a bobbin.

[0067]

The aforementioned carbonization method is applied to the precursor fiber bundle and stabilized fiber bundle of the present invention to obtain a carbon fiber bundle that has excellent mechanical performance.

[0068]

In the carbon fiber bundle of the present invention, the strength of a strand impregnated with a resin is 6000 MPa or more; the strand elastic modulus measured by the ASTM method is 250 to 380 GPa; the ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single fiber perpendicular to the fiber-axis direction is 1.00 to 1.01; a single-fiber diameter is 4.0 to 6.0 μm; and the number of voids having a diameter of 2 nm or more and 15 nm or less and present in the cross-section of a single fiber in the direction perpendicular to the fiber-axis direction is 1 or more and 100 or less. Since the number of voids is as low as 100 or less, a carbon fiber bundle that has extremely high strand strength can be obtained. In particular, in a carbon fiber bundle that has a high elastic modulus, a high strand strength can be developed. More preferably, the number of voids is 50 or less.

[0069]

In a further preferable carbon fiber bundle, the average diameter of voids that satisfies a diameter range from 2 to 15 nm and that are observed in the cross-section of a single fiber perpendicular to the fiber-axis direction is 6 nm or less. The average diameter of 6 nm or less means that a finishing oil agent was uniformly present on a precursor fiber bundle without causing a large amount of local permeation. By ensuring an average diameter of 6 nm or less, the strength of a carbon fiber can be developed stably.

[0070]

In the carbon fiber bundle of the present invention, the sum A (nm^2) of areas of voids present in the cross-section of a single fiber perpendicular to the fiber-axis direction is preferably 2,000 nm^2 or less. Furthermore, voids corresponding to 95% or more of the sum A (nm^2) are preferably present in the area from the surface of a fiber to a depth of 150 nm. The presence of such a structure in a single fiber means that a finishing oil agent is present only immediately near the surface layer in a precursor fiber bundle.

[0071]

In the present invention, the knot tenacity, which is obtained by dividing the tensile breaking stress of a knotted carbon fiber bundle by the cross-sectional area of the fiber bundle (mass and density of a bundle per unit length), is preferably 900 N/mm^2 or more. More preferably, the knot tenacity is 1000 N/mm^2 or more and further preferably, 1100 N/mm^2 or more. The knot tenacity can serve as an index reflecting mechanical performance of a fiber bundle in a direction other than the fiber-axis direction. In particular, performance in the direction perpendicular to the fiber axis can be simply checked by the knot tenacity. In the composite material, since a material is often formed by pseudo-isotropic lamination, a complicated stress field is formed. At this time, other than tensile and

compression stress in the fiber-axis direction, stress is also generated in a direction other than in the fiber-axis direction. Furthermore, if a relatively high-speed strain is produced, as is in an impact test, the state of the stress that is generated within the material is highly complicated. Thus, the strength in a direction different from the fiber-axis direction becomes important. Accordingly, if the knot tenacity is less than 900 N/mm^2, sufficient mechanical performance will not develop in a pseudo-isotropic material.

Examples

[0072]

Now, the present invention will be described in detail by way of Examples. Note that, the performance of fibers in Examples is measured and evaluated in accordance with the following method.

[0073]

[1. Measurement of swelling degree of coagulated fiber]

A fiber bundle that is running in a spinning step is taken. Immediately the fiber bundle is placed in a sealable polyethylene bag and then the bag is stored in a refrigerator of 5°C or less. The time from initiation of storage to completing measurement of the degree of swelling is set to fall within 8 hours.

After weighing a weighing bottle that has been previously dried, is carried out by a direct-reading balance, about 3 g of sample is taken from the fiber bundle and placed in the weighing bottle and measured. The sample is placed in a dewatering cylinder for a desktop centrifuge and placed in the centrifuge. After centrifugal treatment (rough dewatering) is performed at a rotation rate of 3000 rotation/minute for 10 minutes, the dewatered sample is transferred to a weighing bottle and measured. The mass measured herein is regarded as wet mass A.

[0074]

In the case where the roughly dewatered sample still contains a solvent, the sample will be sufficiently washed with water and dewatered. The roughly dewatered sample or the sample that has been further washed and dewatered is transferred to a weighing bottle and dried in a drier of 105°C for 3 hours without a lid. The weighing bottle having the dried sample therein is transferred to a desiccator, gradually cooled for 20 to 30 minutes, and thereafter, the mass of the weighing bottle is measured. The mass measured herein is regarded as dry mass B.

The degree of swelling is measured in accordance with the following expression:

The degree of swelling (%) = (A - B) / B × 100%

[0075]

[2. Method of measuring the degree of swelling of swollen fiber]

Swollen fiber taken in the spinning step is used as a sample and measured in the same manner as the degree of swelling of coagulated fiber is measured.

[0076]

[3. Observation of surface configuration of swollen fiber]

Swollen fiber taken in the spinning step is used as a sample. The solvent contained in the swollen fiber is replaced with t-butanol and the swollen fiber is rapidly frozen with liquid nitrogen. Thereafter, the fiber sample is maintained at a temperature of -30 to -25°C and lyophilized under reduced pressure of about 3 Pa for 24 hours. The fiber sample thus dried is fixed on a sample stand for SEM observation with carbon paste, and then platinum is sputtered to a thickness of about 3 nm with a sputter apparatus. The configuration of the surface is observed by a scanning electron microscope (product name: JSM-7400F manufactured by JEOL Ltd.) at an acceleration voltage of 3 kV and an observation

magnification of 50,000 times.

Voids, i.e., openings of the fiber surface are measured for determining the width in the circumference direction. The number of voids having a width of more than 10 nm is counted. Swollen fibers of 50 or more are subjected to the same measurement. The total number of voids is obtained and the observation area is measured to obtain the average number of voids per unit area (1 μm^2) (average number of openings).

[0077]

[4. Method of measuring fine pore distribution of swollen fiber]

The swollen fiber taken in the spinning step is dried in accordance with the following treatment method. To describe this more specifically, a swollen fiber is fixed to have a predetermined length so that it is not deformed due to shrinkage during the drying process, and is then soaked sequentially in solution mixtures containing water/t-butanol in a ratio of 80/20, 50/50, 20/80, 0/100, each for 30 minutes to replace the solvent contained in the swollen fiber with t-butanol. Subsequently, the swollen fiber sample is placed in a flask and is rapidly frozen in liquid nitrogen. Thereafter, while the temperature of the sample is maintained in the range of -30 to -20°C, the sample is lyophilized under reduced pressure of 100 Pa or less for 24 to 72 hours.

[0078]

The sample of the swollen fiber bundle that has been lyophilized is cut into pieces of about 10 mm in length. About 0.15 g of the swollen fiber pieces are weighed, and a fine pore distribution is measured by a mercury porosimeter (product name: AutoPore IV manufactured by Shimadzu Corporation) under the conditions of atmospheric pressure to a maximum pressure of 30,000 psia. The average fine pore size (nm) is obtained as a volume-average fine pore size, which is fine pore size

weighted by fine pore volume. Furthermore, the total fine pore volume V (ml/g) is obtained from mercury intrusion amount V1 (ml/g) obtained at a pressure corresponding to a fine pore size of 500 nm and mercury intrusion amount V2 (ml/g) obtained at a pressure corresponding to a fine pore size of 10 nm, in accordance with the following expression:

V = V2 - V1

[0079]

[5. Measurement of silicon content of precursor fiber bundle]

[Measuring apparatus]

Fluorescent X-ray spectrometer: product name: ZSX100e manufactured by Rigaku Industrial Corp.,

Target: Rh (end-window type) 4.0 kW,

Dispersive crystal: RX4,

Detector: PC (proportional counter),

Slit: Std.,

Diaphragm: 10 mmϕ,

2θ: 144.681 deg,

Measurement line: Si-Kα,

Excitation voltage: 50 kV,

Exciting current: 70 mA.

[0080]

[Measurement method]

A precursor fiber bundle is uniformly wound around an acrylic resin board of 20 mm in height, 40 mm in length and 5 mm in width, without leaving space, to prepare a measurement sample and is placed in the apparatus. The intensity of fluorescent X-ray of silicon is measured by a conventional fluorescent X-ray analysis method. From the resultant intensity of fluorescent X-ray of silicon of the precursor fiber bundle, the silicon content of the fiber bundle is obtained by use of a calibration curve.

The intensity values of the measured samples (n = 10) are averaged and used as a measurement value.

[0081]

[6. Measurement of uneven surface structure of precursor fiber]

A single fiber of a precursor fiber bundle is fixed at both ends on a metal sample-holder plate applied to a scanning probe microscopic apparatus with carbon paste and measured under the following conditions by the scanning probe microscope. First, the shape image of a single fiber is measured by using a scanning probe microscope. The measured image is subjected to image analysis. Ten cross-section profiles in the direction perpendicular to the fiber-axis are selected and measured to obtain the difference in height (Rp-v) between a highest portion and a lowest portion of a contouring curve and the center-line average roughness Ra. Ten single fibers are subjected to measurement to obtain an average value.

[0082]

[Measurement conditions]

Apparatus: SPI4000 probe station, SPA400 (unit manufactured by SII NanoTechnology Inc.,

Scanning mode: Dynamic force mode (DFM) (shape image measurement),

Probe: SI-DF-20 manufactured by SII NanoTechnology Inc.,

Rotation: 90° (scan in the direction perpendicular to the fiber-axis direction),

Scanning speed: 1.0 Hz,

Number of pixels: 512 × 512,

Measurement environment: Room temperature, in the air.

A single image is obtained per single fiber according to the above conditions and analyzed by image analysis software (SPIWin) under the following conditions.

[0083]

[Image analysis conditions]

The shape image thus obtained is subjected to [flat treatment], [median 8 treatment] and [cubic slope correction]. In this manner, a curved-surface image is corrected to a flat-surface image by fitting correction. The flat-surface image thus corrected is analyzed for surface roughness. The profile of a cross-section in the direction perpendicular to the fiber-axis is measured to obtain the difference in height (Rp-v) between a highest portion and a lowest portion of a contouring curve and to obtain a center-line average roughness Ra.

[0084]

[Flat treatment]

This is a treatment for removing distortion and undulation in the Z-axis direction, that appears in an image data by lift, vibration, creep of a scanner, etc., in other words, a treatment for removing strains of data on SPM measurement caused by an apparatus.

[0085]

[Median 8 treatment]

In a matrix of 3 × 3 around a data-point S to be treated, calculation is performed between S and D1 to D8 to replace Z data of S. In this manner, a filter effect such as smoothing and noise removal is obtained.

In the median 8 treatment, a medium value of Z data of 9 points consisting of S and D1 to D8 is obtained to replace S.

[0086]

[Cubic slope correction]

Slope correction is correction of slope by obtaining a curved surface from all data of the image to be treated by least squares approximation, followed by carrying out fitting of a cubic curved surface. The terms (linear) (quadric) and (cubic) represent dimensions of the curved surface

to be fitted. In the cubic correction, fitting of a cubic curved surface is carried out. Owing to the cubic slope correction, curvature of a fiber from data is eliminated to obtain a flat image.

[0087]

[7. Measurement of X-ray diffraction intensity and crystal orientation degree of stabilized fiber bundle]

A stabilized fiber bundle is cut at arbitrary sites to obtain fiber pieces that are 5 cm in length. Of them, fiber pieces (12 mg) are weighed as sample fiber pieces and unidirectionally arranged such that sample fiber pieces are accurately parallel to the fiber axis. More precisely, a fiber bundle is prepared so as to satisfy the conditions: width, which is the size of the fiber in the direction perpendicular to the longitudinal direction: 2 mm; and thickness, which is the size of the fiber in the direction perpendicular not only to the width direction but also to the longitudinal direction: uniform. The fiber bundle is fixed by impregnating both ends of the fiber bundle with a vinyl acetate/methanol solution, so that the shape of the bundle will not be lost. This is used as the sample fiber bundle to be subjected to measurement.

[0088]

This is fixed on a sample stand for wide-angle X-ray diffraction. The diffraction intensity in the equatorial-line direction is measured by a transmission method to obtain a diffraction intensity profile (the vertical axis: diffraction intensity, the horizontal axis: 2θ (unit: °)). From the obtained profile, diffraction intensity peak-top values in the proximity of 2θ = 17° corresponding to reflection by polyacrylonitrile (100) and 2θ = 25° corresponding to reflection by graphite (002) are detected. The values each are regarded as peak intensity.

[0089]

Furthermore, crystal orientation degree is obtained by measuring

diffraction profile at each of reflection-peak positions in the azimuthal-angle direction to obtain a half band-width "W" of the peak (unit: °) and by calculating in accordance with the following expression.

Degree of crystal orientation (%) = {(180 - W) / 180} × 100

Degree of crystal orientation is measured by taking three sample fiber bundles in the longitudinal direction of the fiber bundle to be measured, measuring a degree of crystal orientation of each of them and obtaining an average value of them.

Note that, X-ray diffraction is measured by a CuKα beam X-ray generation apparatus (using Ni filter) manufactured by Rigaku Corporation (trade name: TTR-III, rotary counter cathode type X-ray generation apparatus) used as an X-ray source. A diffraction intensity profile is detected by a scintillation counter manufactured by Rigaku Corporation. Output is 50 kV-300 mA.

[0090]

[8. Evaluation of the cross-sectional shapes of precursor fiber and carbon fiber]

The ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of each of single fibers that constitute a fiber bundle is determined as follows:

A fiber bundle for measurement is passed through a tube formed of a vinyl chloride resin that has an inner diameter of 1 mm. The tube is then cut in the shape of a circle by a knife to prepare samples. Subsequently, the sample is allowed to adhere to a SEM sample stand so that the cross-section of a fiber faces up; Au is sputtered to a thickness of about 10 nm; and a fiber cross-section is observed by an electron microscope (product name: XL20 scanning type, manufactured by Philips) under the following conditions: an acceleration voltage of 7.00 kV and a migration distance of 31 mm, to measure the major axis and minor axis of

the cross-section of the single fiber.

[0091]

[9. Evaluation of strand physical-property of carbon fiber bundle]

Preparation of a strand test-sample of a carbon fiber bundle impregnated with a resin and measurement of the strength of the sample are performed in accordance with JIS R7608. However, the elastic modulus is calculated in the range of strain in accordance with ASTM.

[0092]

[10. Evaluation of voids in cross-section of carbon fiber bundle]

A single fiber is removed from a carbon fiber bundle. To this, platinum is sputtered on surface of the single fiber to a thickness of 2 to 5 nm by using a sputtering apparatus and then carbon is coated on the resultant single fiber to a thickness of 100 to 150 nm by using a carbon coater apparatus. Thereafter, a tungsten protection film is deposited on the resultant single fiber by using a focused ion beam processing apparatus (product name: FB-2000A manufactured by Hitachi High-Technologies Corporation) to a thickness of about 500 nm. Moreover, etching is performed by using a focused ion beam at an acceleration voltage of 30 kV to obtain a thin piece (thickness: 100 to 150 nm) of fiber having the cross-section.

[0093]

The thin piece (i.e., a cross-section of a single fiber) is observed by a transmission electron microscope (product name: H-7600, manufactured by Hitachi High-Technologies Corporation) under the following conditions: an acceleration voltage of 100 kV and a magnification of 150,000 to 200,000 times.

Furthermore, void portions, which look bright in a TEM image are extracted by using image analysis software (product name: Image-Pro PLUS, manufactured by Nippon Roper K.K.). In this manner, the number

of voids "N" is counted in the overall cross-section and simultaneously the area of each void is measured to obtain an equivalent circle diameter "d" (nm). Furthermore, the sum "A"(nm^2) of areas of voids and average void diameter "D" (nm) are obtained.

[0094]

Furthermore, the depth "T" (nm) of voids is obtained as follows. The area of a void is sequentially and cumulatively calculated from a void near the fiber surface toward a void that is present in the direction of the center of the fiber. When the sum of the above area reaches 95% of area "A," the distance between the position of the last void and the fiber surface is "T." In other words, when a circle is drawn on the cross-section of the single fiber so that the area of all voids that are present between the fiber surface and the circle is 0.95A, and when the radius of the circle is "r" and the radius of the single fiber is "R", then "T" can be obtained in accordance with the following expression:

$T = R - r.$

With respect to 5 fibers, the above measurement is carried out to obtain the average value.

[0095]

[11. Measurement of knot tenacity of carbon fiber bundle]

To both ends of a carbon fiber bundle of 150 mm in length, a grip portion of 25 mm in length is applied to prepare a test sample. In preparing a test sample, a weight of 0.1×10^{-3} N/denier is applied to uni-directionally arranged carbon fiber bundles. In the test sample a single knot is formed virtually at the center. Tension is performed at a crosshead rate of 100 mm/min. A value of knot tenacity is obtained by dividing tensile breaking stress by the cross-sectional area (mass and density of a bundle per unit length) of a fiber bundle. Twelve bundles are used for a test. The smallest value and the largest value are eliminated

and an average value of 10 bundles is used as knot tenacity.

[0096]

(Example 1 and Comparative Examples 1 to 3)

[Preparation of swollen fiber and precursor fiber]

Acrylonitrile and methacrylic acid were polymerized in accordance with an aqueous suspended polymerization to obtain an acrylonitrile-based copolymer formed of an acrylonitrile unit/methacrylic acid unit (98/2 mass %). The resultant polymer was dissolved in dimethyl formamide to prepare a dope having a concentration of 23.5 mass %.

[0097]

The dope was ejected from a spinneret having 2000 ejection holes of 0.13 mm in diameter arranged therein in the air, passed through a space of about 4 mm and then ejected in a coagulant filled with an aqueous solution containing 79.5 mass % dimethyl formamide and controlled at a temperature of 15°C to coagulate and to obtain a coagulated fiber. Subsequently, the coagulated fiber was drawn (1.1 to 1.3 times) in the air and drawn (1.1 to 2.9 times) in a drawing tank filled with an aqueous solution containing 30 mass % dimethyl formamide and controlled at a temperature of 60°C. After the drawing process, the fiber bundle in which a solvent was present was washed with clean water and then drawn (1.2 times to 2.2 times) in hot water of 95°C.

[0098]

Sequentially, to the fiber bundle, a finishing oil agent containing amino-modified silicones as main components was applied so as to apply 1.1 mass %, dried and densified. After the drying and densification step, the fiber bundle was drawn (2.2 times to 3.0 times) between heated rolls of 180°C to further improve the orientation and to perform densification. Thereafter, the bundle was wound to obtain a precursor fiber bundle. The fineness of the precursor fiber was 0.77 dtex. Furthermore, the ratio

of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single fiber was 1.005.

In this case, as the finishing oil agent containing amino-modified silicones as main components, the followings were used.

[0099]

·Amino-modified silicone; KF-865 (mono amino modified side-chain type manufactured by Shin-Etsu Chemical Co., Ltd., viscosity: 110 cSt (25°C), amino equivalent mass: 5,000 g/mol, 85 mass %.

·Emulsifier; NIKKOL BL-9EX (POE (9) lauryl ether, manufactured by Nikko Chemicals Co., Ltd.), 15 mass %.

[0100]

[Stabilization, carbonization treatment]

Next, a plurality of precursor fiber bundles were arranged in parallel and introduced in an oven for stabilization. Air heated to 220°C to 280°C was sprayed to the precursor fiber bundles. In this manner, stabilization of the precursor fiber bundles was performed to obtain stabilized fiber bundles having a density of 1.342 g/cm^3. In this case, 5.0%-extension was performed in the density range of 1.200 g/cm^3 to 1.250 g/cm^3. Furthermore, 1.5%-extension was performed in the density range of 1.250 g/cm^3 to 1.300 g/cm^3. Moreover, -0.5%-extension was performed in the density range of 1.300 g/cm^3 to 1.340 g/cm^3. The total extension rate was set to be 6% and the stabilization time was set to be 70 minutes.

[0101]

Next, the stabilized fiber bundle was fed to a first carbonization furnace having a temperature gradient of 300 to 700°C in nitrogen while the extension rate was increased by 4.5%. The temperature gradient was set to be linear. The treatment time was set to be 1.9 minutes.

[0102]

Furthermore, heat treatment was performed using a second

carbonization furnace in which the temperature gradient was set to be 1000 to 1250°C, in a nitrogen atmosphere at an extension rate of -3.8%. Subsequently, heat treatment was performed using a third carbonization furnace in which the temperature gradient was set to be 1250 to 1500°C, in a nitrogen atmosphere at an extension rate of -0.1% to obtain a carbon fiber bundle. The total extension rate of the carbon fiber bundles through the treatments in the second carbonization furnace and third carbonization furnace was set to be -3.9% and the treatment time was set to be 3.7 minutes.

[0103]

[Surface treatment of carbon fiber]

Subsequently, the bundles were fed to a 10 mass % aqueous ammonium bicarbonate solution. Current was supplied between a carbon fiber bundle serving as an anode and a counter pole so as to obtain a quantity of electricity of 40 coulombs per carbon fiber (1 g) to be treated, washed with warm water of 90°C and then dried. Next, HYDRAN N320 (manufactured by DIC Corporation) was applied in the amount of 0.5 mass % and wound by a bobbin to obtain a carbon fiber bundle. In Example 1 and Comparative Examples 1 to 3, the ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single carbon fiber was 1.005 and the diameter of the fiber was 4.9 μm.

[0104]

[Preparation of uni-direction prepreg]

Onto a mold-releasing paper coated with epoxy resin #410 (that can be cured at 180°C) in the B stage, 156 carbon fibers of the bundle released from a bobbin were uni-directionally arranged and passed through a heat compression roller. In this manner, the carbon fiber bundles were impregnated with epoxy resin. A protecting film was laminated on the resultant fiber bundles to prepare prepregs arranged in a

uni-direction (hereinafter referred to as a "UD prepreg") having a resin content of about 33 mass %, a carbon fiber density of 125 g/m^2 and a width of 500 mm.

[0105]

[Molding of a laminate board and evaluation of mechanical performance]

A laminate board was prepared by using the above UD prepregs and the tensile strength of the laminate board at angle 0° was evaluated by the evaluation method in accordance with ASTM D3039.

The drawing conditions in the spinning step are shown in Table 1.

[0106]

[Table 1]

Table 1

	Spinning conditions							
	Coagulation bath		In the air	Drawing tank (containing warm aqueous solution of organic solvent)			In hot water	Heat drawing
	Tempe-rature (°C)	Conce-ntration (%)	Draw ratio	Tempe-rature (°C)	Conce-ntration (%)	Draw ratio	Draw ratio	Ratio
Example 1	15	79.5	1.1	60	30	3.0	1.2	2.6
Compar.ex.1	15	79.5	1.2	60	30	1.1	2.2	3.0
Compar.ex.2	15	79.5	1.3	60	30	1.7	1.8	2.2
Compar.ex.	15	79.5	1.3	60	30	2.0	1.5	2.6
Example 2	10	79.5	1.1	60	30	2.5	1.4	2.6
Example 3	10	79.5	1.1	60	30	3.0	1.2	2.6
Example 4	5	79.5	1.1	60	30	3.0	1.2	2.6
Example 5	0	79.5	1.1	60	30	3.0	1.2	2.6
Example 6	-5	79.5	1.1	60	30	3.0	1.2	2.6
Example 7	20	79.5	1.1	60	30	3.0	1.2	2.6
Example 8	10	78.0	1.1	60	30	3.0	1.2	2.6
Example 9	10	79.0	1.1	60	30	3.0	1.2	2.6
Example 10	10	81.0	1.1	60	30	3.0	1.2	2.6
Example 11	10	79.5	1.1	50	30	3.0	1.2	2.6
Example 12	10	79.5	1.1	75	30	3.0	1.2	2.6
Example 13	10	79.5	1.1	60	40	3.0	1.2	2.6
Example 14	10	79.5	1.1	70	40	3.0	1.2	2.6
Example 15	10	79.5	1.1	70	60	3.5	1.3	2.8
Example 16	10	79.5	1.1	60	60	3.5	1.3	2.8
Compar.ex.4	10	79.5	1.1	60	20	3.0	1.2	2.6
Compar.ex.5	10	79.5	1.1	35	30	3.0	1.2	2.6
Compar.ex.6	25	79.5	1.1	60	30	3.0	1.2	2.6
Compar.ex.7	15	83.0	1.1	60	30	3.0	1.2	2.6
Compar.ex.8	10	76.0	1.1	60	30	3.0	1.2	2.6
Compar.ex.9	5	77.0	1.1	60	0	2.0	2.0	1.9
Example 29	10	78.5	1.1	60	30	3.0	1.2	2.6
Example 30	10	80.5	1.1	60	30	3.0	1.2	2.6
Example 31	10	79.5	1.1	60	30	3.0	0.99	3.0

[0107]

[Evaluation of fiber]

Measurement of swelling degree of the coagulated fibers and swollen fibers obtained, measurement of surface opening width of swollen fibers, measurement of wide-angle X-ray of the precursor fiber bundles, TMA evaluation, measurement of wide-angle X-ray of the stabilized fiber, measurement of the strand strength and the elastic modulus of carbon fibers, observation of voids in the cross-section of carbon fibers and measurement of knot tenacy were performed. The results are shown in Table 2. It was confirmed that a carbon fiber of Example 1 has high

mechanical performance.

[0108]

[Table 2]

[Table 2-1]

Table 2-1

	Coagulated fiber	Swollen fiber				Precursor fiber bundle			Stabilized fiber bundle		
	Swelling degree	Swelling degree	Average fine pore size	Total fine pore	Average number of pores	Residual amount of Si after extraction	AFM Surface configuration		Wide-angle X-ray diffraction measurement		
	mass %	mass %	nm	ml/g	pores /μ m^2	ppm	Rp-v (nm)	Ra (nm)	B/A	Orientation degree (17°)	Orientation degree (25°)
Example 1	118	74	40.9	0.4	0.4	254	70	7.2	1.39	81.3	79.7
Compar.ex.1	118	90	45	0.48	5.5	458	45	5	1.16	77.8	77.5
Compar.ex.2	118	82	44.1	0.46	5	432	55	6	1.24	77.6	77.9
Compar.ex.3	118	75	43.2	0.46	3.3	305	65	7	1.33	80.2	79
Example 2	115	80	40.3	0.43	1.5	142	61	6.7	1.36	80.8	79.4
Example 3	115	72	38.7	0.41	1.9	137	63	7.1	1.38	81.5	79.8
Example 4	114	70	36.2	0.4	0.6	137	61	6.6	1.37	81.6	79.8
Example 5	110	66	35	0.41	0.6	127	56	6.2	1.36	81.6	79.6
Example 6	100	63	35.1	0.39	0.6	122	51	5.9	1.38	81.7	79.9
Example 7	140	77	39.1	0.43	1	295	90	9.1	1.35	80.9	79.2
Example 8	155	96	54.1	0.54	0.3	117	45	4.2	1.37	81.6	79.8
Example 9	130	84	47.9	0.49	1.8	122	55	6.1	1.36	81.4	79.8
Example 10	115	71	33.4	0.34	2	142	50	5.2	1.35	80.7	79.5
Example 11	115	71	36.7	0.4	1.8	117	59	6.7	1.35	81.3	79.7
Example 12	115	74	40.7	0.4	1.4	127	72	7.9	1.34	81.2	79.7
Example 13	115	69	38.8	0.39	1.1	112	67	7.6	1.34	81.1	79.3
Example 14	115	68	38.1	0.4	1.2	117	75	8.2	1.35	81.2	79.4
Example 15	115	67	39.4	0.42	0.9	122	86	9.3	1.41	82.2	80.2
Example 16	115	67	38.6	0.41	0.5	112	81	8.6	1.42	82.1	80.3
Compar.ex.4	115	81	36.6	0.41	4	315	51	5.2	1.28	80	78.8
Compar.ex.5	115	66	35	0.37	4.8	330	54	5.5	1.25	79.8	78.9
Compar.ex.6	165	90	45.4	0.44	5.2	447	110	11.6	1.25	79.8	78.5
Compar.ex.7	110	69	37	0.28	3.1	315	103	10.4	1.27	79.4	78.1
Compar.ex.8	190	105	69.1	0.63	0.2	40	25	2.5	1.25	79.2	78.2
Compar.ex.9	170	110	58.1	0.57	0.2	49	32	2.9	1.14	77.4	76.9
Example 29	140	86	48	0.48	0.7	128	50	4.7	1.36	81.5	79.8
Example 30	115	71	32.5	0.37	1.8	140	52	5	1.36	81.1	79.6
Example 31	115	70	37.1	0.39	1.7	130	60	6.9	1.38	81.5	79.8

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[Table 2-2]

Table 2-2

	Carbon fiber bundle							Tensile strength of laminate board at 0°
	Strand strength	Strand elastic modulus	Number of voids	Average diameter of voids	Sum of areas	Depth of void	Knot strength	(in terms of 60 vol%)
	MPa	GPa	voids	nm	nm^2	nm	N/mm2	MPa
Example 1	6790	319	66	5.6	1,800	23	1100	3370
Compar.ex.1	5300	320	525	6.3	24,400	168	750	2550
Compar.ex.2	5780	320	284	6.3	8,900	72	800	2800
Compar.ex.3	6410	320	96	5.6	1,900	65	950	3150
Example 2	6670	322	55	5	900	33	980	
Example 3	6880	321	30	4.7	580	25	1080	3500
Example 4	6570	319	35	5.5	830	40	1030	
Example 5	6520	320	37	5.5	850	26	1010	
Example 6	6530	321	33	5.4	820	15	980	
Example 7	6570	322	90	5.6	1750	30	1020	
Example 8	6230	320	21	5.1	440	17	1050	3120
Example 9	6640	321	36	4.8	660	23	1100	3350
Example 10	6430	322	98	5.1	2,100	55	990	
Example 11	6920	321	64	5.2	1,500	45	1070	3520
Example 12	6820	320	13	5.2	310	20	1090	
Example 13	6950	320	37	4.7	680	15	1120	
Example 14	7050	321	50	5.3	1,300	31	1120	3600
Example 15	7110	322	44	5.1	1,100	33	1110	3600
Example 16	7080	322	29	4.5	590	36	1130	
Compar.ex.4	5590	319	400	6.3	6,000	59	780	2710
Compar.ex.5	5850	318	210	6.3	7,500	46	850	2830
Compar.ex.6	5290	321	480	6.4	23,000	182	760	2540
Compar.ex.7	5780	320	220	6.4	8,000	161	790	2780
Compar.ex.8	5700	318	16	5	300	9	860	2800
Compar.ex.9	5850	319	18	5	480	12	820	
Example 29	6580	321	26	5.1	500	21	1060	
Example 30	6620	320	80	5.1	1700	45	1030	
Example 31	6750	320	28	4.6	560	23	1050	

[0109]

(Examples 2 to 16 and Comparative Examples 4 to 9)

Swollen fibers and precursor fiber bundles were obtained in the same manner as in Example 1 except that conditions of the spinning step were partly changed. The fineness of a precursor fiber was set to be 0.77 dtex and the ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single fiber was 1.005. Subsequently, carbon fiber bundles were produced in the same carbonization conditions. The ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single carbon fiber was 1.005 and the diameter of the fiber was 4.9 μm.

The conditions for the spinning step are shown in Table 1 and the evaluation results of individual fiber bundles are shown in Table 2, collectively.

[0110]

(Examples 17 to 20)

Carbon fiber bundles were prepared in the same conditions as in Example 14 by using the precursor fiber bundle obtained in Example 14 except that only heat treatment conditions of the second and third carbonization furnaces were changed. The heat treatment conditions and properties of the carbon fiber bundles are shown in Table 3.

[0111]

[Table 3]

Table 3

Carbon fiber bundle	Example 17	Example 18	Example 19	Example 20
Temperature conditions of second carbonization furnace (°C)	1050-1300	1050-1250	1100-1450	1100-1550
Extension rate in second carbonization furnace (%)	-3.6%	-3.7%	-3.5%	-3.3%
Temperature conditions of third carbonization furnace (°C)	-	1350-1550	1500-1700	1600-1850
Extension rate in third carbonization furnace (%)	-	-0.1%	0.0%	0.5%
Total treatment time in carbonization furnaces (min)	1.9	3.7	3.7	3.7
Major axis/minor axis of cross-section	1.005	1.005	1.005	1.005
Diameter of single fiber (μm)	5.0	4.9	4.8	4.7
Strand strength (MPa)	6300	6550	6300	6150
Strand elastic modulus (GPa)	260	335	355	375
Number of voids N (voids)	56	45	32	24
Average diameter of voids (nm)	5.4	5.1	4.5	3.0
Sum of areas (nm^2)	1400	990	500	210
Depth of void (nm)	31	35	28	16
Knot tenacity (N/mm^2)	1190	1150	1010	950

[0112]

(Examples 21 to 25 and Reference Examples 1 and 2)

A precursor fiber bundle was obtained in the same spinning conditions as in Example 14 except that only the fineness of a single fiber was changed. Carbon fiber bundles were prepared in the same carbonization conditions as in

Example 15 by using the precursor fiber bundle obtained above except that only the heat treatment conditions of the second and third carbonization furnaces were changed. The precursor fibers, heat treatment conditions and properties of carbon fiber bundles are shown in Table 4.

[0113]

[Table 4]

Table 4

Carbon fiber bundle	Example 21	Example 22	Example 23	Example 24	Example 25	Reference Example 1	Reference Example 2
Fineness of single precursor fiber (dtex)	0.52	0.6	0.70	0.9	1.0	0.45	1.1
Temperature conditions of second carbonization furnace (°C)	1000-1250	1000-1250	1000-1250	1000-1250	1000-1250	1000-1250	1000-1250
Extension rate in second carbonization furnace (%)	-3.8%	-3.8%	-3.8%	-3.8%	-3.8%	-3.8%	-3.8%
Temperature conditions of third carbonization furnace (°C)	1250-1400	1250-1430	1250-1450	1250-1550	1250-1600	1250-1380	1250-1650
Extension rate in third carbonization furnace (%)	-0.1%	-0.1%	-0.1%	-0.1%	-0.1%	-0.1%	-0.1%
Total treatment time in carbonization furnaces (min)	3.7	3.7	3.7	3.7	3.7	3.7	3.7
Major axis/minor axis of cross-section	1.005	1.005	1.005	1.005	1.005	1.005	1.005
Strand strength (MPa)	6350	6700	7250	6700	6200	5700	5750
Strand elastic modulus (GPa)	318	320	322	318	317	321	319
Number of voids N (voids)	26	21	39	43	68	35	65
Average diameter of voids (nm)	5.1	4.7	6.1	4.8	5.6	5.0	4.8
Sum of areas (nm^2)	886	510	1200	990	1500	880	1400
Depth of void (nm)	25	30	39	35	32	22	37
Knot tenacity (N/mm^2)	920	1090	1120	1050	950	760	810

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[0114]

(Examples 26 to 28 and Reference Examples 3 and 4)

A precursor fiber bundles was prepared in the same conditions as in Example 14 except that types of amino-modified silicones of finishing oil agents were changed, and subsequently carbon fiber bundles were prepared.

The type of amino-modified silicones used and properties of the precursor fibers and carbon fiber bundles are shown in Table 5.

[0115]

[Table 5]

Table 5

			Example 26	Example 27	Example 28	Reference Example 3	Reference Example 4
Amino-modified silicone	Product No.		KF-868	KF-860	KF-861	KF-393	KF-8004
	Manufacturer		Shin-Etsu Chemical Co., Ltd.	Shin-Etsu Chemical Co., Ltd.	Shin-Etsu Chemical Co., Ltd.	Shin-Etsu Chemical Co., Ltd.	Shin-Etsu Chemical Co., Ltd.
	Type		Mono amino modified side-chain type	Diamino modified side-chain type	Diamino modified side-chain type	Diamino modified side-chain type	Diamino modified side-chain type
	Kinematic viscosity	cSt (25°C)	90	250	3500	70	800
	Amino equivalent weight	g/mol	8800	7600	2000	350	1500
Precursor fiber bundle	Residual Si amount after extraction	ppm	125	105	100	250	190
Carbon fiber bundle	Strand strength	MPa	6980	7060	7100	Production failure, due to winding of fiber in an oven for stabilization	Production failure, due to winding of fiber in an oven for stabilization
	Strand elastic modulus	GPa	321	320	321		
	Number of voids	voids	60	45	20		
	Average diameter of voids	nm	5.4	5.1	4.2		
	Sum of areas	nm^2	1,600	1,100	400		
	Depth of void	nm	28	19	14		
	Knot strength	N/mm^2	1080	1100	1150		

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[0116]

(Examples 29 to 31)

Swollen fibers and precursor fiber bundles were obtained in the same manner as in Example 1 except that the conditions of the spinning step were partly changed. The fineness of the precursor fibers was set to be 0.77 dtex. The ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single fiber was 1.005. Subsequently, carbon fiber bundles were produced in the same carbonization conditions. The ratio of the major axis and the minor axis (major axis/minor axis) of a cross-section of a single carbon fiber was 1.005 and the diameter of the fiber was 4.9 μm.

The conditions of the spinning step are shown in Table 1 and the evaluation results of individual fiber bundles are shown in Table 2.

Industrial Applicability

[0117]

The carbon fiber bundle of the present invention can be used as a constructional material for airplanes, high speed moving bodies, etc.

CLAIMS

1. An acrylonitrile swollen fiber for a carbon fiber having openings of 10 nm or more in width in the circumference direction of the swollen fiber at a ratio in the range of 0.3 openings/μm^2 or more and 2 openings/μm^2 or less on the surface of the swollen fiber, and that is not treated with a finishing oil agent.

2. The swollen fiber according to claim 1, wherein, in a fine pore distribution measured by a mercury press-in method, an average fine pore size is 55 nm or less and a total fine pore volume is 0.55 ml/g or less.

3. The swollen fiber according to claim 1 or 2, wherein a polymer constituting the swollen fiber is an acrylonitrile-based copolymer containing an acrylonitrile unit in an amount of 96.0 mass % or more and 99.7 mass % or less and an unsaturated hydrocarbon unit having at least one carboxyl group or ester group in an amount of 0.3 mass % or more and 4.0 mass % or less as essential components.

4. A method of producing a swollen fiber, including:

(1) a step of preparing a dope at a temperature of 50°C or more and 70°C or less by dissolving an acrylonitrile-based copolymer, which is obtained by copolymerizing acrylonitrile in an amount of 96.0 mass % or more and 99.7 mass % or less and an unsaturated hydrocarbon having at least one carboxyl group or ester group in an amount of 0.3 mass % or more and 4.0 mass % or less, as essential components, in an organic solvent in a concentration in the range of 20 mass % or more and 25 mass % or less;

(2) a step of obtaining a coagulated fiber bundle containing the organic solvent by ejecting the dope from ejection holes into the air by use of a dry-wet spinning method, followed by coagulating in a coagulation bath constituted of an aqueous solution containing an organic solvent in a concentration of 78.0 mass % or more and 82.0 mass % or less, at a temperature of -5°C or more and 20°C or less;

(3) a step of drawing the coagulated fiber bundle in the air at a ratio in the range of 1.0 time or more and 1.25 times or less, followed by further drawing in a

warm aqueous solution containing an organic solvent, a total draw ratio of both drawing processes being 2.6 times or more and 4.0 times or less; and

(4) a step of subsequently removing the solvent with warm water and further drawing in hot water at a ratio of 0.98 times or more and 2.0 times or less.

5. The method according to claim 4, wherein the organic solvent is either dimethyl formamide or dimethyl acetamide.

6. The method according to claim 4 or 5, wherein a draw ratio in the warm aqueous solution is 2.5 times or more and 4.0 times or less.

7. A method of producing a precursor fiber bundle for a carbon fiber by applying a finishing oil agent containing silicone compounds as main components to a bundle of the swollen fiber according to any of claims 1 to 3.

8. A method of producing a stabilized fiber bundle including feeding the precursor fiber bundle obtained by the method according to claim 7 to a hot-air circulation type oven for stabilization at a temperature of 220 to 260°C for 30 minutes or more and 100 minutes or less, thereby applying heat treatment at an extension rate of 0% or more and 10% or less under an oxidizing atmosphere, and the method satisfying the following conditions:

(1) intensity ratio (B/A) of peak A ($2\theta = 25°$) and peak B ($2\theta = 17°$) in the equatorial-line direction, which is determined by wide angle x-ray diffraction measurement of the fiber bundle, is 1.3 or more,

(2) orientation degree of peak B is 80% or more,

(3) orientation degree of peak A is 79% or more, and

(4) density is 1.335 g/cm^3 or more and 1.360 g/cm^3 or less.

9. The method of producing the stabilized fiber bundle according to claim 8, wherein extension treatment is separately performed in at least three sets of conditions: an extension rate of 3.0% or more and 8.0% or less at a fiber density in the range of 1.200 g/cm^3 or more and 1.260 g/cm^3 or less; an extension rate at 0.0% or more and 3.0% or less at a fiber density in the range of 1.240 g/cm^3 or more and 1.310 g/cm^3 or less; and an extension rate of -1.0% or more and 2.0% or less at a fiber density in the range of 1.300 g/cm^3 or more and 1.360 g/cm^3 or less.