

(19)



(11)

EP 3 808 880 A1

(12)

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

(43) Date of publication:

21.04.2021 Bulletin 2021/16

(51) Int Cl.:

D01F 9/22^(2006.01) D01F 6/18^(2006.01)

(21) Application number: **1982232.5**

(86) International application number:

PCT/JP2019/023851

(22) Date of filing: **17.06.2019**

(87) International publication number:

WO 2019/244830 (26.12.2019 Gazette 2019/52)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(72) Inventors:

- **OKUDA, Haruki**
Iyo-gun, Ehime 791-3193 (JP)
- **WATANABE, Jun**
Iyo-gun, Ehime 791-3193 (JP)
- **MATSUMOTO, Naohiro**
Iyo-gun, Ehime 791-3193 (JP)
- **TANAKA, Fumihiko**
Iyo-gun, Ehime 791-3193 (JP)

(30) Priority: **18.06.2018 JP 2018115112**

18.06.2018 JP 2018115113

30.08.2018 JP 2018161056

(74) Representative: **Mewburn Ellis LLP**

**Aurora Building
Counterslip
Bristol BS1 6BX (GB)**

(71) Applicant: **Toray Industries, Inc.**

Tokyo, 103-8666 (JP)

(54) **CARBON FIBER AND METHOD FOR PRODUCING SAME**

(57) The invention aims to provide a carbon fiber that hardly suffers fractures during molding for producing a carbon fiber reinforced composite and serves to provide a carbon fiber reinforced composite having a high elastic modulus. The carbon fiber has a strand elastic modulus of 360 GPa or more, a strand strength of 3.5 GPa or more, and a single-fiber diameter of 6.0 μm or more, and further satisfying either or both of the requirements (a) and (b) specified below: (a) when one end is fixed end and the other end being free end which is capable of rotation about the axis of the fiber bundle, the residual twist count is 2 turns/m or more, and (b) the total fineness, which is the product of the single fiber fineness (g/km) and the filament number (number) of the carbon fiber, is 740 g/km or more. Furthermore, the carbon fiber meets

the relationship represented by formula (1) wherein Es (GPa) is the single-fiber elastic modulus and A (N) is the loop fracture load: $A \geq -0.0017 \times E_s + 1.02$... formula (1). Or the carbon fiber has a single-fiber diameter of 6.0 μm or more, satisfies the relationship represented by formula (2) wherein E (GPa) is the strand elastic modulus and B (MPa) is the knot strength determined under conditions where the heat loss rate is 0.15% or less at 450°C, and has a twist count of 20 to 80 turns/m:

$$B \geq 6.7 \times 10^9 \times E^{-2.85} \dots \text{formula (2).}$$

EP 3 808 880 A1

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to carbon fiber and a method for the production thereof.

BACKGROUND ART

10 **[0002]** Carbon fibers have high specific strength and specific modulus and can serve as reinforcing fibers for carbon fiber reinforced composites to realize large weight reduction in producing members, and accordingly, they are used in a wide range of fields as essential material for constructing a highly energy-efficient society. Recently, they have been in wider use in such fields as automobiles and electronic equipment housing where there is a strong call for cost reduction, and manufacturers are now strongly required to realize a reduction in cost for final member production including the molding cost.

15 **[0003]** In order to effectively reduce the cost of final members, it is important not only to achieve a cost reduction for the carbon fiber itself but also to take a comprehensive approach including creation of carbon fibers showing enhanced performance to ensure a decreased consumption and development of molding methods with increased efficiency, thereby realizing a reduction in the overall molding cost.

20 **[0004]** However, when trying to decrease the consumption of carbon fiber while maintaining a required stiffness as one of the important characteristics of the final member, for example, simple application of an existing high modulus carbon fiber often fails in realizing a reduction in the cost of the final member production. This is because existing high modulus carbon fibers are low in productivity and tend to be expensive and also because they are low in moldability and require large total processing costs to provide final members. The moldability of the carbon fiber depends on features related to handleability and processability in various steps performed to provide the final member, including, for example,

25 the handleability of fiber bundles and the degree of fuzz generation, as well as the easiness of piecing yarns for the replacement of carbon fiber bobbins in the case of continuous production of a carbon fiber reinforced composite. **[0005]** In recent years, furthermore, carbon fibers are in wider use in the form of discontinuous fibers, particularly in cases where an emphasis is placed on reducing costs. In general, when carbon fibers are used as discontinuous fibers, the lengths of the carbon fibers tend to be shortened as they are sheared and folded in the molding process. This tendency is noticeable in the case of existing high modulus carbon fibers and the adoption of carbon fibers with high tensile modulus does not always serve effectively to provide high-stiffness final members.

30 **[0006]** In the case of polyacrylonitrile based carbon fiber, which is the most widely used carbon fiber, the industrial production process includes a stabilization step for converting precursor fibers for carbon fiber into stabilized fibers in an oxidizing atmosphere at 200°C to 300°C and a carbonization step for carbonizing them in an inert atmosphere of 300°C to 2,000°C. In the case of polyacrylonitrile based high modulus carbon fiber, the industrial production process includes a graphitization step for further graphitizing them in an inert atmosphere at or below a maximum temperature of 3,000°C. Such a graphitization step can effectively increase the tensile modulus of the carbon fibers, but on the other hand, it tends to require equipment that is resistant to high temperatures or lead to final carbon fibers having poor tensile strength or compressive strength as a result of accelerated crystal growth in the carbon fibers. Thus, when such a high modulus carbon fiber material is employed, the productivity of carbon fibers in the aforementioned forms will be low and the moldability in producing carbon fiber reinforced composites will be also low. And their fiber lengths will be decreased in the case where they are used in the form of discontinuous fibers.

35 **[0007]** Several methods have also been proposed to increase the tensile modulus of carbon fibers by techniques other than graphitization. As one of them, a method to develop a high tension in a carbon fiber production process has been proposed.

40 **[0008]** Patent documents 1 and 2 propose techniques in which the molecular weight of a polyacrylonitrile copolymer is controlled so that fuzz generation is suppressed even if a high tension is developed in the carbonization step.

[0009] Patent document 3 proposes a technique in which the strand elastic modulus is increased by performing high-degree stretching in the stabilization step and the pre-carbonization step.

45 **[0010]** Furthermore, precursor fiber bundles for carbon fiber are entangled in the techniques proposed in Patent documents 4 to 7 or twisted in those proposed in Patent documents 8 and 9 in order to realize an increased processability in the carbonization step.

50 **[0011]** Patent document 10 proposes a technique in which the gauge length dependency of pre-carbonized fiber bundles is controlled by entanglement or twisting during carbonization under high tension so that deterioration in the adhesion between carbon fibers and matrix is prevented while ensuring an increased strand elastic modulus of the carbon fiber to be obtained.

55 **[0012]** Patent document 11 proposes a high moldability carbon fiber having a high knot strength in spite of a large single-fiber fineness, which is produced by controlling the copolymerization composition of precursor fiber bundles for

carbon fiber.

[0013] In addition, Patent document 12 proposes a carbon fiber that suffers little deterioration in mechanical properties in spite of a large single fiber diameter, which is produced in a similar way.

5 PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0014]

10

Patent document 1: International Publication WO2008/047745

Patent document 2: Japanese Unexamined Patent Publication (Kokai) No. 2009-256833

Patent document 3: International Publication WO2008/063886

Patent document 4: Japanese Unexamined Patent Publication (Kokai) No. 2001-49536

15

Patent document 5: Japanese Unexamined Patent Publication (Kokai) No. HEI-10-195718

Patent document 6: Japanese Unexamined Patent Publication (Kokai) No. 2000-160436

Patent document 7: Japanese Unexamined Patent (Kokai) No. SHO-47-026964

Patent document 8: Japanese Unexamined Patent Publication (Kokai) No. SHO-56-091015

Patent document 9: Japanese Unexamined Patent Publication (Kokai) No. 2002-001725

20

Patent document 10: Japanese Unexamined Patent Publication (Kokai) No. 2014-141761

Patent document 11: International Publication WO2013/157613

Patent document 12: International Publication WO2013/157612

SUMMARY OF INVENTION

25

PROBLEMS TO BE SOLVED BY THE INVENTION

[0015] These conventional techniques, however, have problems as described below.

30

[0016] In Patent documents 1 and 2, the molecular weight of the polyacrylonitrile copolymer is controlled, but it does not serve to significantly improve the critical orientation tension in the carbonization step, and a large increase in the strand elastic modulus cannot be expected.

[0017] In Patent document 3, although the stretching ratio is high in and before the pre-carbonization step, the stretching ratio is low in the carbonization step, which should serve for easy improvement in the strand elastic modulus of carbon fiber, and accordingly a large increase in the strand elastic modulus cannot be expected.

35

[0018] Patent documents 4 to 9 pay no attention to increasing the stretching ratio in the carbonization step and describe no idea of focusing on it.

[0019] Patent document 10 describes that the strand elastic modulus, adhesion to the matrix, and strand strength can be simultaneously maintained at high levels, and that a high processability is achieved in the carbonization step. However, no attention is paid to the moldability in producing a carbon fiber reinforced composite or the fiber breakage that may occur during use in the form of discontinuous fibers, and there is no description about the idea of focusing on them.

40

[0020] Patent documents 11 and 12 pay no particular attention to the stretching ratio in the carbonization step, and in some examples, the strand elastic modulus is increased to 343 GPa maximum by raising the carbonization temperature. Although not described, in the conventional approach of raising the carbonization temperature, the moldability in producing carbon fiber reinforced composites tends to be low as in the case of commercial carbon fibers of high modulus grades. Furthermore, no attention is paid to the fiber breakage that may occur during use in the form of discontinuous fibers, and there is no description about the idea of focusing on it.

45

[0021] In summary, the documents proposing the conventional techniques contain no description of a method by which the tensile modulus and moldability of carbon fibers and, in addition, the ease of maintaining required fiber lengths during use as discontinuous fibers are simultaneously maintained at high levels, but simultaneous realization of them at high levels has been an important issue in achieving a reduction in the total cost of final member production.

50

MEANS OF SOLVING THE PROBLEMS

55

[0022] In order to meet the above object, a first embodiment of the carbon fiber according to the present invention provides a carbon fiber having a strand elastic modulus of 360 GPa or more, a strand strength of 3.5 GPa or more, and a single-fiber diameter of 6.0 μm or more, and further satisfying either the requirement (a) or (b) specified below:

(a) when one end is fixed end and the other end being free end which is capable of rotation about the axis of the

fiber bundle, the residual twist count is 2 turns/m or more, and
 (b) the total fineness, which is the product of the single-fiber fineness (g/km) and the filament number (number) of the carbon fiber, is 740 g/km or more.

5 **[0023]** In addition, a second embodiment of the carbon fiber according to the present invention provides a carbon fiber meeting the relationship represented by formula (1), wherein E_s (GPa) is the single-fiber elastic modulus and A (N) is the loop fracture load:

10
$$A \geq -0.0017 \times E_s + 1.02 \quad \text{formula (1)}$$

[0024] In addition, a third embodiment of the carbon fiber according to the present invention provides a carbon fiber having a single-fiber diameter of 6.0 μm or more, satisfying the relationship represented by formula (2) wherein E (GPa) is the strand elastic modulus and B (MPa) is the knot strength determined under conditions where the heat loss rate is 0.15% or less at 450°C, and having a twist count of 5 to 80 turns/m:

15
$$B \geq 6.7 \times 10^9 \times E^{-2.85} \quad \text{formula (2)}$$

20 **[0025]** The method for producing the carbon fiber according to the present invention, furthermore, includes a step in which a precursor fiber bundle for carbon fiber is subjected to stabilization treatment in an air atmosphere in the temperature range of 200°C to 300°C, a step for pre-carbonization in which the resulting stabilized fiber bundle is heat-treated in an inert atmosphere at or below a maximum temperature of 500°C to 1,000°C until the density reaches 1.5 to 1.8 g/cm³, and a step for carbonization in which the resulting pre-carbonized fiber bundle is heat-treated in an inert atmosphere, the precursor fiber bundle for carbon fiber having a single-fiber fineness of 0.9 dtex or more, having a tension controlled at 5 mN/dtex or more during the carbonization treatment, and meeting either the following requirement (c) or (d):

- 25 (c) the fiber bundle to be subjected to the carbonization treatment has a twist count of 2 turns/m or more, and
 30 (d) the total fineness, which is the product of the single-fiber fineness (g/km) and the filament number (number), of the resulting carbon fiber is 740 g/km or more.

ADVANTAGEOUS EFFECTS OF THE INVENTION

35 **[0026]** The carbon fiber according to the present invention is a carbon fiber that has both a high tensile modulus and a high moldability in composite production and easily maintains a required fiber length even when used in the form of discontinuous fibers. The carbon fiber according to the present invention serves effectively for reducing the required consumption of carbon fibers, increasing the productivity in composite production, and producing a composite having improved mechanical properties.

DESCRIPTION OF PREFERRED EMBODIMENTS

40 **[0027]** For the present invention, both a single fiber and an aggregate thereof of carbon fiber are simply referred to as carbon fiber. For the present invention, examples of such an aggregate of single fibers of carbon fiber include bundles, webs, composites thereof, and others in various forms. A method for producing the carbon fiber according to the present invention will be described later.

[0028] For the present invention, the term "tensile modulus" collectively refers to the single-fiber elastic modulus determined by single-fiber tensile test of carbon fiber and the strand elastic modulus determined by the method described later. The relation between the single-fiber elastic modulus and the strand elastic modulus will be described later.

50 **[0029]** The first embodiment of the carbon fiber according to the present invention provides a carbon fiber having a strand elastic modulus of 360 GPa or more, a strand strength of 3.5 GPa or more, and a single-fiber diameter of 6.0 μm or more, and further satisfying either the requirement (a) or (b) specified below. Here, it is preferable to satisfy both (a) and (b).

- 55 (a) When one end is fixed end and the other end being free end which is capable of rotation about the axis of the fiber bundle, the residual twist count is 2 turns/m or more.
 (b) The total fineness, which is the product of the single-fiber fineness (g/km) and the filament number (number) of

the carbon fiber, is 740 g/km or more.

[0030] Each requirement will be described below.

[0031] In the first embodiment of the carbon fiber according to the present invention, the strand elastic modulus is 360 GPa or more. The strand elastic modulus is preferably 370 GPa or more, more preferably 380 GPa or more, still more preferably 400 GPa or more, and still more preferably 440 GPa or more. A higher strand elastic modulus allows the carbon fiber to serve more effectively to increase the stiffness of the resulting carbon fiber-reinforced composite, making it easier to obtain a high-stiffness carbon fiber-reinforced composite. If the strand elastic modulus is 360 GPa or more, it has a large industrial value because it serves to produce a carbon fiber-reinforced composite having a greatly increased stiffness. From the viewpoint of producing a high-stiffness carbon fiber-reinforced composite, the strand elastic modulus of carbon fiber is preferably as high as possible, but in the case of conventional carbon fibers, an excessively high strand elastic modulus tends to lead to a decreased moldability in producing carbon fiber-reinforced composites or a decreased fiber length during use in the form of discontinuous fibers. The strand elastic modulus can be determined according to the tensile test of resin-impregnated strands specified in JIS R7608 (2004). An evaluation method for the strand elastic modulus will be described later. There are various known methods that serve to control the strand elastic modulus, but for the present invention, it is preferable to control it by changing the tension in the carbonization treatment step.

[0032] In the first embodiment of the carbon fiber according to the present invention, the strand strength is 3.5 GPa or more. The strand strength is preferably of 3.7 GPa or more, more preferably 3.9 GPa or more, and still more preferably 4.3 GPa or more. In general, a higher strand strength tends to serve for producing a carbon fiber-reinforced composite having a higher tensile strength, thus leading to a high-performance fiber reinforced composite. A carbon fiber having an extremely low strand strength may lead to a decrease in moldability in producing a carbon fiber-reinforced composite, but in many cases, serious problems will not occur if it is 3.5 GPa or more. The strand strength can be determined according to the tensile test of resin-impregnated strands specified in JIS R7608 (2004). An evaluation method for the strand strength will be described later. There are various known methods that serve to control the strand strength, but in the case where the conventional method of raising the carbonization temperature is used, the strand strength often decreases with an increasing strand elastic modulus. A carbon fiber having a strand strength of 3.5 GPa or more in spite of a high strand elastic modulus can be produced by the method for producing the carbon fiber according to the present invention, which will be described later.

[0033] In the first embodiment of the carbon fiber according to the present invention, the single-fiber diameter is 6.0 μm or more. The single-fiber diameter is preferably 6.5 μm or more, and more preferably 6.9 μm or more. In general, a larger single-fiber diameter makes it more difficult to maintain both the strand elastic modulus and the strand strength at high levels, but according to the first embodiment of the carbon fiber according to the present invention, both of them can be maintained at high levels as described above even when the single-fiber diameter is 6.0 μm or more. Furthermore, a larger single-fiber diameter ensures a higher moldability because it serves to prevent fuzz generation and fuzz accumulation on guide parts such as rollers from being caused by the friction between carbon fibers being unwound from the bobbin or their friction with the guide parts in the step for producing a carbon fiber-reinforced composite. For the first embodiment of the carbon fiber according to the present invention, there is no particular limitation on the upper limit of the single-fiber diameter, but if it is too large, the strand strength and the strand elastic modulus will easily decrease, and accordingly, it is considered that the upper limit is practically about 15 μm . In addition, it is also preferable that the single-fiber diameter is 7.4 μm or less from the viewpoint of easily maintaining both the strand elastic modulus and the strand strength at high levels. Although a method for determining the single-fiber diameter will be described later, it may be calculated from the specific gravity, the metsuke, and the filament number of the fiber bundle or may be determined by scanning electron microscopy. If the measurement device to be used is correctly calibrated, substantially the same results can be obtained by any method. If the cross-sectional shape of the single fiber being observed by scanning electron microscopy is not a perfect circle, the equivalent circle diameter is used instead. The equivalent circle diameter is the diameter of a perfect circle having a cross-sectional area equal to the measured cross-sectional area. The single-fiber diameter can be controlled by changing the rate of discharge from the spinneret during spinning of the precursor fiber bundle for carbon fiber or the stretching ratio in appropriate steps.

[0034] The first embodiment of the carbon fiber according to the present invention provides a carbon fiber having a strand elastic modulus, a strand strength, and a single-fiber diameter as specified above and satisfying one or more of the requirements specified below:

(a) when one end is fixed end and the other end being free end which is capable of rotation about the axis of the fiber bundle, the residual twist count is 2 turns/m or more, and

(b) the total fineness, which is the product of the single-fiber fineness (g/km) and the filament number (number) of the carbon fiber, is 740 g/km or more.

[0035] Satisfying either or both of the requirements (a) or (b) enables the prevention of deterioration in moldability

even when the strand elastic modulus is high, thus realizing high industrial values.

[0036] For the first embodiment of the carbon fiber according to the present invention, the residual twist count is preferably 2 turns/m or more, more preferably 5 turns/m or more, still more preferably 10 turns/m or more, still more preferably 16 turns/m or more, still more preferably 20 turns/m or more, still more preferably 30 turns/m or more, and still more preferably 46 turns/m or more.

[0037] For the present invention, a fixed end means an appropriate portion of a fiber bundle that is fixed so that it cannot rotate about the length direction of the fiber bundle, which is assumed to be the axis, and can be realized by restraining the rotation of the fiber bundle using adhesive tape or the like. For the present invention, a free end means the end that comes out when a continuous fiber bundle is cut in the cross-sectional direction, which is perpendicular to the length direction, and is not fixed to anything to allow the fiber bundle to rotate about its length direction, which is assumed to be the axis. For the present invention, the residual twist means the permanent twist of a carbon fiber bundle left with one end fixed and the other free, and is represented in the number of turns per meter. A semi-permanent twist means a twist that will not unravel naturally without the application of an external force. For the present invention, if a twisted specimen remains unraveled after being left for 5 minutes in a specific arrangement as described in the relevant Examples with one end fixed and the other free, such a twist is defined as a semi-permanent twist, or a residual twist. If the residual twist count is 2 turns/m or more, it will be easy to maintain a high moldability even when the strand elastic modulus is high. The mechanism of this has not been clarified quantitatively, but qualitatively, it is considered to be as follows. Specifically, in the case of a carbon fiber having a residual twist count of 2 turns/m or more, it is considered that the twist can work to fix the relative positions of single fibers in the fiber bundle, and therefore, the single fibers in the fiber bundle tend to remain undamaged by the friction between fiber bundles and their friction with guide parts or the like. If the residual twist count is 5 turns/m or more, furthermore, fuzz generation is suppressed and accordingly, a high tension can be developed in the carbonization step, serving effectively to increase the strand elastic modulus. In addition, if the residual twist count is 20 turns/m or more, fuzz generation is suppressed strongly to enable the control of the alignment of fiber bundles, and as a result, smooth stress transfer can occur between fiber bundles, easily causing enhancement in the knot strength, which will be described later. For a fiber bundle mounted with one end fixed and the other free, the residual twist count can be controlled by a known method. Specifically, the residual twist count can be controlled by adjusting the twist count of the fiber bundle in the carbonization step.

[0038] As described previously, for the first embodiment of the carbon fiber according to the present invention, the total fineness is preferably 740 g/km or more, more preferably 850 g/km or more, still more preferably 1,300 g/km or more, still more preferably 1,600 g/km or more, and still more preferably 2,000 g/km or more. A total fineness of 740 g/km or more makes it easy to maintain a high moldability even when the strand elastic modulus is high. The mechanism of this has not been clarified quantitatively, but qualitatively, it is considered to be as follows. Specifically, in the case of a carbon fiber having a total fineness of 740 g/km or more, it is considered that the single fibers present in the outermost layer of a fiber bundle that are susceptible to damage by friction as described above account for a smaller proportion of the total number of single fibers in the fiber bundle, leading to a smaller degree of damage by friction suffered by the entire fiber bundle. The total fineness is the product of the single-fiber fineness (g/km) and the filament number (number) and therefore, it can be controlled by changing the single-fiber fineness or the filament number.

[0039] The second embodiment of the carbon fiber according to the present invention provides a carbon fiber meeting the relationship represented by formula (1), wherein E_s (GPa) is the single-fiber elastic modulus and A (N) is the loop fracture load:

$$A \geq -0.0017 \times E_s + 1.02 \quad \text{formula (1)}$$

[0040] The constant in formula (1) is preferably 1.04 more, more preferably 1.06 more, still more preferably 1.08 more, and particularly preferably 1.10 more. The loop fracture load means the weight working on a single fiber at the time it fractures as it is gradually bent in a loop-like shape, and it is determined by the method described later. Furthermore, the single-fiber elastic modulus means the tensile modulus of a single fiber in a carbon fiber material and has a correlation with the strand elastic modulus described previously. For the present invention, as described in detail later, the single-fiber elastic modulus can be determined by carrying out single-fiber tensile test for a plurality of gauge lengths, calculating the slope of the stress strain curve measured for each of the gauge lengths, and removing the influence of the compliance of the measuring system in consideration of gauge length dependency. In general, an increase in the single-fiber elastic modulus often leads to a decrease in the loop fracture load. If the loop fracture load is small, the carbon fibers will be broken easily in a molding step in which discontinuous fibers receive a force in the bending direction, and the shortening of the fiber length deteriorates the advantage of producing a fiber reinforced composite having an increased stiffness. As the loop fracture load increases, the single fibers become more resistant to the force in the bending direction and accordingly, the fiber length will not be shortened significantly in a molding step in which discontinuous fibers receive a

large force in the bending direction, thus serving effectively to produce a fiber reinforced composite having an increased stiffness. If the loop fracture load A and the single-fiber elastic modulus E_s satisfy the relation represented by formula (1), the carbon fiber is resistant to a force in the bending direction even when the high single-fiber elastic modulus is high, and the carbon fiber, used in the form of discontinuous fibers, serves efficiently to produce a carbon fiber reinforced composite having an increased stiffness. A carbon fiber that satisfies the relation represented by formula (1) can be produced by the method for producing the carbon fiber according to the present invention, which will be described later. Furthermore, it is preferable that a carbon fiber according to the first embodiment of the present invention also satisfies the requirements of the second embodiment. Even if the strand elastic modulus is high, such a carbon fiber can not only effectively prevent a decrease in moldability, but also maintain the fiber length when used in the form of discontinuous fibers, thus enabling easy production of a high-performance carbon fiber-reinforced composite.

[0041] For the second embodiment of the carbon fiber according to the present invention, the single-fiber elastic modulus is preferably 360 GPa or more, more preferably 370 GPa or more, still more preferably 380 GPa or more, still more preferably 400 GPa or more, and still more preferably 440 GPa or more. In the case of the conventional carbon fibers, a higher single-fiber elastic modulus leads to a decrease in the loop fracture load, and the fiber length are easily shortened during their molding in the form of discontinuous fibers, whereas in the case of the second embodiment of the carbon fiber according to the present invention, the loop fracture load is large relative to the single-fiber elastic modulus and accordingly, a carbon fiber reinforced composite having largely increased stiffness can be produced in spite of a high single-fiber elastic modulus. The single-fiber elastic modulus can be increased in the same way as for the strand elastic modulus.

[0042] In the third embodiment of the carbon fiber according to the present invention provides a carbon fiber having a single-fiber diameter of 6.0 μm or more, satisfying the relationship represented by formula (2) wherein E (GPa) is the strand elastic modulus and B (MPa) is the knot strength determined under conditions where the heat loss rate is 0.15% or less at 450°C, and having a twist count of 5 to 80 turns/m:

$$B \geq 6.7 \times 10^9 \times E^{-2.85} \quad \text{formula (2)}$$

[0043] In the third embodiment of the carbon fiber according to the present invention, the single-fiber diameter is 6.0 μm or more. The single-fiber diameter is preferably 6.5 μm or more, and more preferably 6.9 μm or more. In general, a larger single-fiber diameter makes it more difficult to maintain both the strand elastic modulus and the knot strength at high levels, but according to the third embodiment of the carbon fiber according to the present invention, both of them can be maintained at high levels even when the single-fiber diameter is 6.0 μm or more. Furthermore, a larger single-fiber diameter ensures a higher moldability because it serves to prevent fuzz generation from being caused by the friction between carbon fibers being unwound from the bobbin or their friction with the guide parts such as rollers. For the third embodiment of the carbon fiber according to the present invention, there is no particular limitation on the upper limit of the single-fiber diameter, but if it is too large, the knot strength and the strand elastic modulus will easily decrease, and accordingly, it is considered that the upper limit is practically about 15 μm . In addition, it is also preferable that the single-fiber diameter is 7.4 μm or less from the viewpoint of easily maintaining both the strand elastic modulus and the knot strength at high levels.

[0044] In the third embodiment of the carbon fiber according to the present invention, the tensile modulus E (GPa) of resin-impregnated strands and the knot strength B (MPa) determined under conditions where the heat loss rate is 0.15% or less at 450°C satisfy the relationship represented by formula (2):

$$B \geq 6.7 \times 10^9 \times E^{-2.85} \quad \text{formula (2)}$$

[0045] For the present invention, the heat loss rate at 450°C, which will be described in detail later, is calculated from the difference in the mass of a carbon fiber specimen between before and after heating it for 15 minutes in an oven filled with nitrogen at a temperature of 450°C. The knot strength is an indicator that reflects the mechanical properties of a fiber bundle in directions other than the fiber axial direction. When producing a composite, a carbon fiber bundle receives bending stress in directions other than the fiber axis direction, and the knot strength affects the fuzz generation, which represents fiber fractures that occur during the composite production process. Fuzz is commonly generated if the running speed of the fiber bundle is increased during the production of a composite in an attempt to realize efficient production of a composite, but an increase in the knot strength serves to produce a high quality composite even when the running speed of the fiber bundle is high. The knot strength tends to be improved by applying a sizing agent to the carbon fiber bundle. On the other hand, in such cases where the molding temperature of the matrix is so high that the sizing agent may undergo thermal degradation to cause a decrease in the adhesion strength between the carbon fiber and the matrix,

it may be desirable to avoid the application of a sizing agent from the viewpoint of ensuring an improved adhesion strength. For the present invention, therefore, the knot strength of a carbon fiber bundle in an unsized state is used as an evaluation indicator. Specifically, the term "determination under conditions where the heat loss rate is 0.15% or less at 450°C" means that an unsized fiber bundle is used for evaluation or the sizing agent is removed before evaluation in the case where it is sized and has a heating loss rate of more than 0.15% at 450°C. Removal of a sizing agent may be carried out by a generally known method such as, for example, using a solvent that dissolves the sizing agent. If the knot strength is low, fuzz tends to be generated during the molding step to produce a carbon fiber-reinforced composite, possibly leading to a decrease in the moldability. In general, an increase in the strand elastic modulus tends to cause a decrease in the knot strength. If the strand elastic modulus and the knot strength satisfy the relationship represented by formula (2), both the strand elastic modulus and the knot strength can be balanced at high levels. The proportionality constant in formula (2) is preferably 6.9×10^9 , and more preferably 7.2×10^9 . A carbon fiber that satisfies formula (2) which represents the relationship between the strand elastic modulus and the knot strength can be produced by the method for producing the carbon fiber according to the present invention, which will be described later.

[0046] Furthermore, it is preferable that a carbon fiber according to the first embodiment of the present invention also satisfies the requirements of the third embodiment and/or the second embodiment. Even if the strand elastic modulus is high, such a carbon fiber can effectively prevent a decrease in moldability. In particular, in the case where yarn piecing is required in the molding step, it is advantageous for continuous production because the yarn-pieced portions will not be fractured easily.

[0047] For the third embodiment of the carbon fiber according to the present invention, the twist count is 5 and 80 turns/m. If the twist count is in the above range, fuzz generation is suppressed strongly to enable the control of the alignment of fiber bundles, and as a result, smooth stress transfer can occur between fiber bundles, easily causing enhancement in the knot strength. From the viewpoint of enhancing the handleability in the molding step, it is preferable for the twist count in the third embodiment to be 20 to 80 turns/m.

[0048] In the case where the carbon fiber according to the present invention is in the form of a carbon fiber bundle, it is preferable that the twist angle of the carbon fiber bundle surface layer is 2.0° to 30.5°. The twist angle of the carbon fiber bundle surface layer means the angle between the fiber axial direction of the single-fibers present in the outermost layer of the carbon fiber bundle and the long axis direction of the whole carbon fiber bundle, and it may be directly observed, but can be calculated more precisely from the twist count, the filament number, and the single-fiber diameter as described later. If the twist angle is controlled in the above range, fuzz generation is suppressed, and therefore, a high tension can be applied in the carbonization step to ensure an effective increase in the strand elastic modulus. For the present invention, the twist angle of the carbon fiber bundle surface layer is preferably 4.8° to 30.5°, more preferably 4.8° to 24.0°, still more preferably 4.8° to 12.5°, and still more preferably 4.8° to 10.0°. A carbon fiber bundle having a twist angle in the above range can be produced by the method for producing the carbon fiber according to the present invention described later. Specifically, the twist angle of the carbon fiber bundle surface layer can be controlled by adjusting the twist count of the fiber bundle and, in addition, adjusting the filament number and the single-fiber diameter in the carbonization step. As the filament number and single-fiber diameter of a carbon fiber bundle are increased, a larger twist angle can be maintained if the twist count of the fiber bundle is constant, thereby enhancing the effect of twisting.

[0049] For the carbon fiber according to the present invention, it is preferable that the crystallite size L_c (nm) and the orientation parameter of crystallites π_{002} (%) satisfy the relationship represented by formula (3).

$$\pi_{002} \geq 4.0 \times L_c + 73.2 \quad \text{formula (3)}$$

[0050] The crystallite size L_c is an indicator representing the thickness in the c-axis direction of the crystallites present in the carbon fiber. In general, it is determined by observing the fiber bundle by wide-angle x-ray diffraction, but it may also be determined by separately observing each of three single fibers by microbeam wide-angle x-ray diffraction and averaging the measurements to give the average crystallite size L_c (s). To determine the average crystallite size L_c (s) in the case where the size of the microbeam is equal to or smaller than the single-fiber diameter, measurements taken at a plurality of points aligned in the diameter direction of a single fiber are averaged to give an evaluation value to represent that single fiber, and such values obtained in the same manner from a total of three single fibers are averaged and adopted. The evaluation technique will be described in detail later. It is noted that the wide-angle x-ray diffraction data of a single fiber is essentially the same as the generally known wide-angle x-ray diffraction data of a fiber bundle, and the average crystallite size L_c (s) is nearly the same as the crystallite size L_c . Studies by the present inventors have shown that the orientation parameter of crystallites π_{002} tends to increase with an increasing crystallite size L_c , and formula (3) empirically shows an upper limit assumed on the basis of existing data on carbon fibers. In general, as the crystallite size L_c increases, the strand elastic modulus also increases, but the strand strength, knot strength, loop

fracture load, and moldability in producing a carbon fiber-reinforced composite often tend to decrease. In addition, the orientation parameter of crystallites π_{002} strongly affects the strand elastic modulus, and the strand elastic modulus increases with an increasing orientation parameter of crystallites. The fact that the orientation parameter of crystallites π_{002} satisfies the relationship represented by formula (3) means that the orientation parameter of crystallites π_{002} is large relative to the crystallite size L_c , and even when the strand elastic modulus is high, it will be possible to effectively prevent a decrease in the strand strength, knot strength, loop fracture load, and moldability, thereby realizing high industrial values. For the present invention, the constant in formula (3) is preferably 73.5, and still more preferably 74.0. A carbon fiber that satisfies the relationship represented by formula (3) can be produced by increasing the orientation tension in the carbonization step.

[0051] For the carbon fiber according to the present invention, the crystallite size L_c is preferably 2.2 to 3.5 nm, more preferably 2.4 to 3.3 nm or more, still more preferably 2.6 to 3.1 nm or more, and particularly preferably 2.8 to 3.1 nm. A crystallite size L_c of 2.2 nm or more ensures effective stress bearing inside the carbon fiber to allow the single-fiber elastic modulus to be increased easily, whereas a crystallite size L_c of 3.5 nm or less serves to prevent stress concentration to ensure high levels of the strand strength, knot strength, loop fracture load, and moldability. The crystallite size L_c can be controlled by changing the treatment time and maximum temperature mainly in the carbonization step.

[0052] For the carbon fiber according to the present invention, the orientation parameter of crystallites π_{002} is preferably 80.0% to 95.0%, more preferably 80.0% to 90.0%, and still more preferably 82.0% to 90.0%. The orientation parameter of crystallites π_{002} is an indicator representing the orientation angle with respect to the fiber axis of crystallites present in carbon fiber. As in the case of the crystallite size, it may also be determined by separately observing each of three single fibers by microbeam wide-angle x-ray diffraction and averaging the measurements to give the average orientation parameter of crystallites π_{002} (s). To determine the average orientation parameter of crystallites π_{002} (s) in the case where the size of the microbeam is equal to or smaller than the single-fiber diameter, measurements taken at a plurality of points aligned in the diameter direction of a single fiber are averaged to give an evaluation value to represent that single fiber, and such values obtained in the same manner from a total of three single fibers are averaged and adopted. The evaluation technique will be described in detail below. It is noted that the wide-angle x-ray diffraction data of a single fiber is essentially the same as the generally known wide-angle x-ray diffraction data of a fiber bundle, and the average orientation parameter of crystallites π_{002} (s) is nearly the same as the orientation parameter of crystallites π_{002} . A orientation parameter of crystallites of 80.0% or more makes it is easy to maintain a high strand elastic modulus. The orientation parameter of crystallites π_{002} (s) can be controlled by changing the orientation tension in addition to the temperature and time of the carbonization step.

[0053] For the carbon fiber according to the present invention, it is preferable that the strand elastic modulus E (GPa) and the crystallite size L_c (nm) satisfy the relationship represented by formula (4).

$$E \times L_c^{-0.5} \geq 200 \text{ (GPa/nm}^{0.5}) \quad \text{formula (4)}$$

[0054] As a result of studies by the present inventors, it has been found that both the strand elastic modulus and the moldability are easily maintained at particularly high levels when carbon fiber satisfies formula (4). The reason for the fact that the strand elastic modulus and the moldability are easily maintained at high levels when formula (4) is satisfied has not been clarified yet, but it is speculated as follows. Specifically, as can be seen in the Hall-Petch equation, which is widely used in the field of polycrystalline materials, if the -0.5 th power of the crystallite size L_c is assumed to be an indicator of some kind of toughness of the material, it can be interpreted that a larger $L_c^{-0.5}$ indicates a tougher material whereas a smaller $L_c^{-0.5}$ indicates a brittle material. Therefore, when formula (4) is satisfied, it means that the product of the strand elastic modulus and the toughness of the material is equal to or larger than a certain value and suggests that the strand elastic modulus and the toughness of the material are maintained at high levels. Such a carbon fiber that satisfies formula (4) can be produced by increasing the orientation tension in the carbonization step.

[0055] For the carbon fiber according to the present invention, it is preferable that the surface oxygen concentration O/C is 0.05 to 0.50. The surface oxygen concentration is an indicator representing the number of oxygen-containing functional groups introduced in the surface of a carbon fiber and can be determined by photoelectron spectroscopy, which will be described later. A higher surface oxygen concentration serves to achieve a larger increase in the adhesion between the carbon fiber and the matrix and production of a carbon fiber-reinforced composite having better mechanical properties. It is more preferable for the surface oxygen concentration O/C to be 0.07 to 0.30. If the surface oxygen concentration O/C is 0.05 or more, a sufficiently strong adhesion to the matrix is achieved, whereas if it is 0.50 or less, it serves to prevent the peeling of the surface of the carbon fiber due to excessive oxidation, thereby leading to a carbon fiber-reinforced composite having improved mechanical properties. Methods for controlling the surface oxygen concentration O/C in the above range will be described later.

[0056] In the case where the carbon fiber according to the present invention is in the form of a carbon fiber bundle, it

is preferable that the filament number is preferably 10,000 or more. The filament number is more preferably 15,000 or more, and still more preferably 20,000 or more. If the twist count is constant, a larger filament number ensures a larger distance between the central axis of the twist and the outer periphery of the fiber bundle. Accordingly, the twist is stabilized easily, and fuzz generation and fracture are suppressed easily even when a high tension is applied in the carbonization step, thereby effectively realizing an increase in the strand elastic modulus and an increase in the moldability.

[0057] A method for producing the carbon fiber according to the present invention is described below.

[0058] A precursor fiber bundle for carbon fiber serving as a material for producing the carbon fiber according to the present invention can be prepared by spinning a spinning dope solution of a polyacrylonitrile copolymer.

[0059] Examples of the polyacrylonitrile copolymer include not only homopolymer prepared from acrylonitrile alone, but also copolymers produced from other monomers in addition to acrylonitriles as main components. Specifically, it is preferable that a polyacrylonitrile copolymer contains 90 to 100% by mass of acrylonitrile and less than 10% by mass of a copolymerizable monomer.

[0060] Useful monomers that are copolymerizable with acrylonitrile include, for example, acrylic acid, methacrylic acid, itaconic acid, alkali metal salts thereof, ammonium salts, lower alkyl esters, acrylamide, derivatives thereof, allyl sulfonic acid, methallylsulfonic acid, and salts or alkyl esters thereof.

[0061] A spinning dope solution is prepared by dissolving a polyacrylonitrile copolymer as described above in a solvent, such as dimethyl sulfoxide, dimethyl formamide, and dimethyl acetamide, nitric acid, aqueous solutions of zinc chloride, and aqueous solutions of sodium rhodanide, that can dissolve the polyacrylonitrile copolymer. In the case where the solution polymerization technique is used for preparing a polyacrylonitrile copolymer, it is preferable to use the same solvent for both polymerization and spinning because it eliminates the necessity of steps for separating the resulting polyacrylonitrile copolymer and re-dissolving it in a spinning solvent.

[0062] A precursor fiber bundle for carbon fibers can be produced by spinning a spinning dope solution prepared as described above by a wet or dry-jet wet spinning technique.

[0063] The spinning dope solution is coagulated by introducing it into a coagulation bath, and the resulting coagulated fiber bundle is passed through a water washing step, an underwater stretching step, an oil agent treatment step, and a drying step, thereby providing a precursor fiber bundle for carbon fiber. The water washing step may be omitted to send the coagulated fiber bundle directly to the underwater stretching step, or the water washing step may be carried out to remove the solvent before the underwater stretch step. In general, it is preferable for the underwater stretching step to be carried out in a single or multiple stretching baths that are controlled at temperatures of 30°C to 98°C. Furthermore, a dry heat stretching step or a steam stretching step may be added to the above steps.

[0064] It is preferable for the precursor fiber bundle for carbon fiber to have a single-fiber fineness of 0.9 dtex or more, more preferably 1.0 dtex or more, and still more preferably 1.1 dtex or more. A precursor fiber bundle for carbon fiber having a higher single-fiber fineness ensures less frequent fracture generation in the fiber bundle due to contact with the rollers and guide parts and stabler implementation of the steps for spinning, carbon fiber stabilization, pre-carbonization, and carbonization. If the single-fiber fineness of the precursor fiber bundle for carbon fiber is 0.9 dtex or more, it allows the process stability to be maintained easy. If the single-fiber fineness of the precursor fiber bundle for carbon fiber is too high, it will be difficult sometimes to perform uniform treatment in the stabilization step and it will cause a decrease in the stability of the production process, possibly leading to a carbon fiber bundle and a carbon fiber having deteriorated mechanical properties. The single-fiber fineness of the precursor fiber bundle for carbon fiber can be controlled by known techniques such as changing the rate of spinning dope solution discharge from the spinneret, the stretching ratio, etc.

[0065] The resulting precursor fiber bundle for carbon fiber is normally in the form of continuous fibers. Here, the filament number per fiber is preferably 1,000 to 80,000. For the present invention, a plurality of precursor fiber bundles for carbon fiber may be combined as required to adjust the filament number per fiber of the carbon fiber to be produced.

[0066] The carbon fiber according to the present invention can be produced by subjecting the aforementioned precursor fiber bundle for carbon fiber to stabilization treatment, pre-carbonization treatment, and carbonization treatment in this order.

[0067] The stabilization treatment of the precursor fiber bundle for carbon fiber is preferably carried out in an air atmosphere at a temperature ranging from 200°C to 300°C. The precursor fiber bundle for carbon fiber is subjected to stabilization treatment to provide a stabilized fiber bundle.

[0068] For the present invention, the aforementioned stabilization treatment is followed by pre-carbonization of the stabilized fiber bundle. In the pre-carbonization step, it is preferable for the stabilized fiber bundle resulting from the stabilization treatment step to be subjected to heat treatment in an inactive atmosphere at or below a maximum temperature of 500°C to 1,000°C until the density reaches 1.5 to 1.8 g/cm³. The stabilized fiber bundle is then subjected to the pre-carbonization treatment step to provide a pre-carbonized fiber bundle.

[0069] In addition, the aforementioned pre-carbonization step is followed by carbonization of the pre-carbonized fiber bundle. In the carbonization step, the pre-carbonized fiber bundle resulting from the pre-carbonization treatment step is subjected to the carbonization treatment step in an inactive atmosphere. The maximum temperature in the carbonization

treatment step is preferably 1,500°C or more, and more preferably 2,300°C or more. The maximum temperature in the carbonization treatment step is preferably as high as possible from the viewpoint of providing a carbon fiber having a high strand elastic modulus and a high single-fiber elastic modulus, but if the maximum temperature is at least 1,500°C or more, it ensures the production of a carbon fiber that is high not only in the strand elastic modulus and single-fiber elastic modulus, but also in the knot strength and loop fracture load. If the carbonization temperature is too high, on the other hand, the knot strength and loop fracture load tend to decrease, and for the carbonization step, therefore, it is recommended that an appropriate maximum temperature is adopted to allow the required strand elastic modulus and single-fiber elastic modulus to be in good balance with the knot strength and loop fracture load. The carbon fiber according to the present invention can easily realize these physical properties in good balance even when the maximum temperature in the carbonization step is 2,300°C.

[0070] For the present invention, furthermore, the tension in the carbonization step is 5 mN/dtex or more, preferably 5 to 18 mN/dtex, more preferably 7 to 18 mN/dtex, and particularly preferably 9 to 18 mN/dtex. The tension in the carbonization step is calculated by dividing the tension (mN) measured at the outlet of the carbonization furnace by the total fineness (dtex), which is the product of the single-fiber fineness (dtex) and filament number of the precursor fiber bundle for carbon fiber used. Adjusting the tension in the above range allows the orientation parameter of crystallites π_{002} to be controlled appropriately without significantly affecting the crystallite size L_c of the resulting carbon fiber, and enables the production of a carbon fiber satisfying the relationship represented by the aforementioned formula (1) and/or formula (2). From the viewpoint of increasing the strand elastic modulus and the single-fiber elastic modulus of the carbon fiber, the tension is preferably as high as possible, but if it is too high, it may cause a decrease in the processability in the carbonization step and deterioration in the quality of the resulting carbon fiber, and therefore, it is preferable that an appropriate tension is adopted in light of both of them.

[0071] For the method for producing the carbon fiber according to the present invention, it is more preferable that the method for producing the carbon fiber further satisfies either of the following requirements (c) and (d). It is still more preferable that both requirements (c) and (d) are satisfied.

(c) The fiber bundle to be subjected to the carbonization treatment has a twist count of 2 turns/m or more.

(d) The total fineness, which is the product of the single-fiber fineness (g/km) and the filament number (number), of the resulting carbon fiber is 740 g/km or more.

[0072] Satisfying either of the requirements (c) or (d) enables the production of a carbon fiber having high moldability in spite of a high strand elastic modulus.

[0073] For the carbon fiber according to the present invention, the fiber bundle has a twist number of 2 turns/m or more in the carbonization treatment step. The twist number is preferably 5 turns/m or more, more preferably 10 turns/m or more, still more preferably 16 turns/m or more, still more preferably 30 turns/m or more, and still more preferably 46 turns/m or more. Although there is no particular limitation on the upper limit of the twist count, it is effective to control it about 60 turns/m or less in order to increase the productivity and the stretching limit in the carbonization step. If the twist number is controlled in the above range, fuzz generation is suppressed in the carbon fiber production process to realize the application of a high tension, thus enabling easy production of a carbon fiber having a high strand elastic modulus and a high single-fiber elastic modulus. The twist number of the fiber bundle in the carbonization treatment step means the twist count possessed by the fiber bundle being treated for carbonization. If the tension in the carbonization step is increased without giving a twist, there may occur fractures of single fibers and increased fuzz generation to cause a decrease in the processability in the carbonization step or fractures of the whole fiber bundle, possibly making it impossible to maintain a required tension. The twist count can be controlled by a method in which a precursor fiber bundle for carbon fiber, stabilized fiber bundle, or pre-carbonized fiber bundle is once wound up on a bobbin and then a bobbin is rotated in the plane perpendicular to the direction of unwinding the fiber bundle, or a method in which, instead of winding up on a bobbin, rotating rollers, belts, etc., are brought into contact with the traveling fiber bundle to give a twist.

[0074] For the present invention, the filament number of the fiber bundle in the carbonization treatment step is preferably 10,000 or more, more preferably 15,000 or more, and still more preferably 20,000 or more. If the twist count of the fiber bundle in the carbonization treatment step is constant, a larger filament number ensures a larger distance between the central axis of the twist and the outer periphery of the fiber bundle to allow the twist to serve more easily to suppress fuzz generation, thereby more effectively producing a carbon fiber having a higher single-fiber elastic modulus. There is no particular limitation on the upper limit of the filament number, and an appropriate upper limit may be adopted in light of the intended use.

[0075] For the present invention, examples of the inert gas used for the inert atmosphere include nitrogen, argon, and xenon, of which nitrogen is preferable from an economical point of view.

[0076] The carbon fiber bundle produced by the above production method may be further subjected to additional graphitization treatment in an inert atmosphere at or lower than 3,000°C to appropriately adjust the single-fiber elastic modulus in light of the intended use.

[0077] It is preferable that the carbon fiber bundle thus produced is subjected to surface treatment after the carbonization treatment step to introduce oxygen-containing functional groups in order to increase the strength of adhesion between the carbon fiber and the matrix. Useful surface treatment methods include gas phase oxidization, liquid phase oxidization, and liquid phase electrolytic oxidization, of which liquid phase electrolytic oxidization has been preferred from the viewpoint of high productivity and uniform treatment. For the present invention, there is no specific limitation on the technique to be used for liquid phase electrolytic oxidization and a generally known one may be selected appropriately. For the electrolytic surface treatment to perform the liquid phase electrolytic oxidization, the amount of current is preferably 2 to 100 c/g, and more preferably 2 to 80 c/g. If the amount of current during the electrolytic surface treatment is 2 c/g or more, a sufficient number of oxygen-containing functional groups are introduced to the surface of the carbon fiber to easily realize a required adhesiveness to the resin and prevent a decrease in the elastic modulus of the composite, whereas if it is 100 c/g or less, it serves to prevent the electrolytic surface treatment from causing flaw formation on the surface of the carbon fiber and prevent a decrease in the loop fracture load.

[0078] Performing surface treatment such as electrolytic surface treatment serves to introduce oxygen-containing functional groups into the carbon fiber bundle and control the surface oxygen concentration O/C of the carbon fiber bundle. To control the surface oxygen concentration O/C in the preferable range for the present invention, the amount of current and the treatment time for the surface treatment may be adjusted by known methods.

[0079] After the electrolytic treatment, a sizing agent may also be attached in order to further enhance the handleability and high-order workability of the resulting carbon fiber bundle or increase the strength of adhesion between the carbon fiber and the matrix. An appropriate sizing agent may be adopted to suit the type of the matrix used in the carbon fiber-reinforced composite. In addition, the amount of agent etc. may be finely adjusted from the viewpoint of handleability and high-order processability. Furthermore, in such cases where the molding temperature of the matrix is so high that the sizing agent may undergo thermal degradation to cause a decrease in the strength of adhesion between the carbon fiber and the matrix, it may be desirable to minimize the amount of the sizing agent to be attached or avoid the implementation of sizing treatment.

[0080] The methods used for measuring the various physical properties described herein are described below. The evaluations were made based on one measurement ($n = 1$) unless otherwise specified.

<Strand strength and strand elastic modulus of carbon fiber>

[0081] The strand strength and strand elastic modulus of a carbon fiber are determined by the following procedure according to JIS R7608 (2004) "Resin-impregnated strand test method". It is noted that in the case where the fiber bundle of carbon fiber has a twist, evaluations are made after unraveling the twist by twisting it in the reverse rotation direction by the same number of turns as its original twist count. The resin mixture used consisted of Celloxide (registered trademark) 2021 P (manufactured by Daicel Chemical Industries, Ltd.), boron trifluoride monoethylamine (manufactured by Tokyo Chemical Industry Co., Ltd.), and acetone at a ratio of 100/3/4 (parts by mass), and the curing conditions used included atmospheric pressure, a temperature of 125°C, and test time of 30 minutes. Ten strands formed of carbon fiber bundles are examined and the measurements taken are averaged to represent the strand strength and the strand elastic modulus. Here, the strain should be in the range 0.1% to 0.6% when determine the strand elastic modulus.

<Average of single fiber diameter of carbon fiber>

[0082] A cross section of a single fiber of a carbon fiber sample is observed by scanning electron microscopy to examine its cross-sectional features. The diameter of a perfect circle that has the same cross-sectional area as the observed one is calculated and adopted as the diameter of the single fiber. A total of 50 single fibers ($N = 50$) are examined and their diameters are averaged and adopted. Here, the acceleration voltage is set to 5 keV.

[0083] It is noted that the scanning electron microscope used for the Examples given herein was an S-4800 scanning electron microscope (SEM) manufactured by Hitachi High-Technologies Corporation.

<Residual twist count measured with one end fixed and the other free>

[0084] A guide bar is installed at a height of 60 cm from a horizontal surface, and an appropriate portion of a carbon fiber bundle is taped to the guide bar to serve as a fixed end, followed by cutting the carbon fiber bundle at a position 50 cm away from the fixed end to create a free end. The free end is enclosed in a folded piece of tape so that the fiber bundle will not unraveled into single fibers. To eliminate that part of a twist which is not semi-permanent, that is, temporal or releasable over time, the specimen is left in this state for 5 minutes and the free end is rotated while counting the number of turns, followed by recording the number of turns n (turns) required for complete untwisting. The residual twist count is calculated by the following formula. The above measuring procedure is performed three times repeatedly and the results are averaged to represent the residual twist count for the present invention.

$$\text{Residual twist count (turns/m)} = n \text{ (turns)} / 0.5 \text{ (m)}$$

<Single-fiber elastic modulus of carbon fiber>

[0085] The single-fiber elastic modulus of a carbon fiber is determined as described below according to JIS R7606 (2000). First, a carbon fiber bundle of about 20 cm is divided into approximately four equal portions, and single fibers are sampled from the four bundles one by one in turn so that specimens are collected as evenly as possible from the entire bundle. The single fibers sampled are secured to pasteboard sheets having holes of 10, 25, or 50 mm. For the securing, an epoxy based adhesive (Araldite (registered trademark), fast curing type, manufactured by Nichiban Co., Ltd.) is used, and after application, it is allowed to stand at room temperature for 24 hours to ensure sufficient curing. Each pasteboard sheet with a secured single fiber is mounted on a tensile test machine, and tensile test was performed on 15 specimens under the conditions of a gauge length of 10, 25, or 50 mm and a strain rate of 40%/min. In the stress (MPa) - strain (%) curve of each single fiber, the slope (MPa/%) is determined in the strain range of 0.3% to 0.7%, and the apparent single-fiber elastic modulus is calculated by the formula given below.

$$\text{Apparent single-fiber elastic modulus (GPa)} = \text{slope (MPa/\%)} \text{ in the strain range of } 0.3\% - 0.7\% / 10$$

Then, for each of the gauge lengths 10, 25 and 50 mm, the average single-fiber elastic modulus E_{app} (GPa) is calculated, and its reciprocal, i.e., $1/E_{\text{app}}$ (GPa^{-1}), on the vertical axis (Y-axis) is plotted against the reciprocal of the gauge length L_0 (mm), i.e., $1/L_0$ (mm^{-1}), on the horizontal axis (X-axis). The reciprocal of the intercept of the curve on the y-axis shows the single-fiber elastic modulus corrected for compliance, and this value is adopted as the single-fiber elastic modulus for the present invention.

[0086] It is note that the tensile tester used for the Examples given herein was a Tensilon RTF-1210 tensile tester manufactured by A&D Company, Limited.

<Loop fracture load>

[0087] A single fiber with a length of about 10 cm is placed on a glass slide, and 1 to 2 drops of glycerin are put onto the central portion. Then, both ends of the single fiber is twisted slightly in the fiber's circumferential direction to form a loop in the central portion of the single fiber, and a cover glass is put on the loop. This is mounted on the stage of a microscope and recorded on video under the conditions of a total magnification of 100 times and a frame rate of 15 frames/sec. With the stage occasionally adjusted to maintain the loop within the field of view, both ends of the looped fiber are pulled in the opposite directions at a constant rate while pressing them against the glass slide in order to strain the single fiber until it is fractured. The video is viewed by frame-by-frame playback to identify the frame just before loop fracture, and the width W of the loop just before loop fracture is determined by image analysis. The single-fiber diameter d is divided by W to calculate the d/W ratio. The test was performed on 20 specimens ($n = 20$), and the average d/W ratio is multiplied by the single-fiber elastic modulus E_s to calculate the loop strength as $E_s \times d/W$. In addition, it is multiplied by the cross-sectional area $\pi d^2/4$ determined from the single-fiber diameter and $\pi E_s \times d^3/4W$ is adopted as the loop fracture load.

<Heating loss rate at 450°C of carbon fiber bundle>

[0088] A carbon fiber bundle being examined is cut to a mass of 2.5 g and wound up on a reel having a diameter of about 3 cm, and its mass w_0 (g) before the heat treatment is determined. Then, it is heated in a nitrogen atmosphere in an oven at a temperature of 450°C for 15 minutes, and allowed to cool to room temperature in a desiccator, followed by determining its mass w_1 (g) after heating. The heating loss rate at 450°C is calculated by the following formula. Here, three measurements are taken and their average is adopted.

$$\text{Heating loss rate (\%)} \text{ at } 450^\circ\text{C} = (w_0 - w_1) / w_0 \times 100 \text{ (\%)}$$

<Knot strength of carbon fiber bundle>

[0089] Carbon fiber bundles with a heating loss rate at 450°C of 0.15% or less were used for the measurement of the

EP 3 808 880 A1

knot strength. When evaluating a carbon fiber bundle treated with a sizing agent, the carbon fiber bundle was cleaned in acetone to remove the sizing agent and used after drying. The dried carbon fiber bundle is subjected to measurement of its heating loss rate at 450°C and cleaning is repeated until it becomes 0.15% or less.

5 **[0090]** In the case where the carbon fiber bundle has a twist, evaluations are made after unraveling the twist by twisting it in the reverse rotation direction by the same number of turns as its original twist count. A carbon fiber bundle as described above having a length of 150 mm is divided or combined with others to form a carbon fiber bundle having a total fineness of 7,000 to 8,500 dtex, and the resulting carbon fiber bundle is used for measurement. It is noted that the total fineness of a carbon fiber bundle means the product of the average fineness (dtex) of the single fibers in the carbon fiber bundle and the filament number. A grip with a length of 25 mm is attached to each end of this carbon fiber bundle to prepare a test specimen, and during this test specimen preparation, a load of 0.1×10^{-3} N/denier is applied to parallel the carbon fibers. One knot is formed at the center of the test specimen, and fiber bundle tensile test is performed with a crosshead speed of 100 mm/min maintained while it is pulled. Measurements are taken from a total of 12 fiber bundles, and after eliminating the largest and smallest ones, the remaining the 10 measurements are averaged and used to represent them. Then the standard deviation of the 10 values is calculated and used as the standard deviation of knot strength. To calculate the knot strength to be used, the largest load obtained in the tensile test is divided by the average cross-sectional area of the carbon fiber bundles.

<Twist angle of carbon fiber bundle surface layer>

20 **[0091]** The overall diameter (μm) of a carbon fiber bundle is calculated first by the following formula from the single-fiber diameter (μm) and the filament number described above, and the twist angle ($^\circ$) of the carbon fiber bundle surface layer is calculated by the following formula using the twist count (turn/m).

25 Overall diameter of carbon fiber bundle (μm) = {(the single-fiber diameter)² × filament number}^{0.5}

30 Twist angle ($^\circ$) of carbon fiber bundle surface layer = atan (overall diameter of fiber bundle × $10^{-6} \times \pi \times$ twist count)

<Crystallite size Lc and orientation parameter of crystallites π_{002} of carbon fiber bundle>

35 **[0092]** The fibers in a carbon fiber bundle being examined are paralleled and bound using a collodion-alcohol solution to prepare a test specimen of a square prism having a length of 4 cm and a base of 1 mm × 1 mm. The test specimen prepared is examined by wide angle x-ray diffraction under the following conditions.

1. Measurement of crystallite size Lc

40 **[0093]**

- X-ray source: CuK α beam (tube voltage 40 kV, tube current 30 mA)
- Detector: goniometer + monochromator + scintillation counter
- Scanning range: $2\theta = 10^\circ$ - 40°
- Scan mode: Step scan, unit step 0.02° , counting time 2 sec

45 **[0094]** In the diffraction pattern obtained, the half-width of the peak appearing in the vicinity of $2\theta = 25^\circ$ to 26° is measured, and the crystallite size is calculated from this value by the following Scherrer equation.

50
$$\text{Crystallite size (nm)} = K\lambda / \beta_0 \cos\theta_B$$

wherein

55
$$K = 1.0, \lambda = 0.15418 \text{ nm (wavelength of X-ray)}$$

EP 3 808 880 A1

$$\beta_0 = (\beta_E^2 - \beta_1^2)^{1/2}$$

β_E : apparent half-width (measured) (rad), β_1 : 1.046×10^{-2} (rad)

θ_B : Bragg diffraction angle

2. Measurement of orientation parameter of crystallites π_{002}

[0095] The crystal peak described above is scanned in the circumferential direction to determine the intensity distribution and calculation is performed from its half width by the formula given below.

$$\pi_{002} = (180 - H) / 180$$

wherein

H: apparent half-width (deg)

[0096] The above measuring procedure is performed three times repeatedly and the measurements taken are arithmetically averaged to give the crystallite size and the orientation parameter of crystallites of the carbon fiber bundle.

[0097] In the Examples and Comparative examples given below, XRD-6100 manufactured by Shimadzu Corporation was used as the wide-angle x-ray diffraction apparatus.

<Average crystallite size Lc (s) and average orientation parameter of crystallites π_{002} (s) of single fiber of carbon fiber>

[0098] Single fibers are randomly sampled from a carbon fiber bundle and examined by wide angle x-ray diffraction using an instrument that can generate an X-ray μ -beam. For the measurement, a microbeam with a wavelength of 0.1305 nm that is shaped to 3 μ m in the fiber axis direction and 1 μ m in the fiber diameter direction is used to scan the single fiber in 1 μ m steps in the fiber diameter direction. The irradiation time is 2 seconds in each step. The camera length, which is the distance between the detector and the specimen, is set within the range of 40-200 mm. The camera length and the coordinate position of the beam center are determined from measurements taken by using cerium oxide as standard sample. A two dimensional diffraction pattern recorded after removing the specimen is subtracted from the observed two dimensional diffraction pattern to remove the dark noise attributed to the detector and the scattering noise attributed to air to provide a corrected two-dimensional diffraction pattern. The corrected two-dimensional diffraction patterns obtained from different positions in the fiber diameter direction of the single fiber are added together to provide an averaged two dimensional diffraction pattern in the fiber diameter direction of the single fiber. In this averaged two dimensional diffraction pattern, sector integration is performed over the angle range of $\pm 5^\circ$ around a direction perpendicular to the fiber axis to provide a diffraction intensity profile in the 2θ direction. The diffraction intensity profile in the 2θ direction is least-squares fitted using two Gaussian functions to calculate the angle $2\theta_m$ ($^\circ$), which is the 2θ value where the diffraction intensity is at a maximum, and the full width at half maximum FWHM ($^\circ$) of the composite function of the two Gaussian functions. In addition, circumferential integration is performed over the range of $\pm 5^\circ$ around the angle $2\theta_m$ ($^\circ$) where the diffraction intensity profile in the 2θ direction is at a maximum to obtain a diffraction intensity profile in the circumferential direction. The diffraction intensity profile in the circumferential direction is least-squares fitted using a Gaussian function to calculate the full width at half maximum FWHM $_\beta$ ($^\circ$). The crystallite size Lc (s) and the orientation parameter of crystallites π_{002} (s) of the single fiber is determined by the formula given below, and the results from three single fibers are averaged to calculate the average crystallite size Lc (s) and the average orientation parameter of crystallites π_{002} (s).

$$Lc (s) (nm) = K\lambda / FWHM\cos(2\theta_m/2)$$

Here, Scherrer factor K is 1.0 and the X-ray wavelength λ is 0.1305 nm. The full width at half maximum FWHM and $2\theta_m$, both in degrees ($^\circ$), are used after conversion into values in radian (rad).

$$\pi_{002} (s) (\%) = (180 - FWHM_\beta) / 180 \times 100 (\%)$$

[0099] For the Examples given herein, the second hatch of SPring-8 Beamline BL03XU (FSBL) was used as the facility that can generate X-ray μ -beam and a C9827DK-10 flat panel detector (pixel size 50 μ m \times 50 μ m) manufactured by

Hamamatsu Photonics K.K. was used as the detector.

<Surface oxygen concentration O/C of carbon fiber>

5 **[0100]** The surface oxygen concentration O/C of a carbon fiber bundle can be determined by X-ray photoelectron spectroscopy according to the procedure described below. First, dirt etc. attached on the surface of a carbon fiber bundle is removed with a solvent, and it is cut to about 20 mm and spread on a specimen support table made of copper. Then, the specimen support table is placed in a specimen chamber, and the pressure in the specimen chamber is maintained at 1×10^{-8} Torr. Subsequently, measurements are taken using $AlK\alpha_{1,2}$ as X-ray source and assuming a photoelectron takeoff angle of 90° . Here, for perform peak correction for electrification that occurs during measurement, the value of binding energy of the C_{1s} primary peak (peak top) is adjusted to 286.1 eV, and the C_{1s} peak area can be determined by drawing a straight baseline in the range of 282 to 296 eV. Furthermore, the O_{1s} peak area can be determined by drawing a straight baseline in the range of 528 to 540 eV. Here, the surface oxygen concentration is calculated from the ratio between the O_{1s} peak area and the C_{1s} peak area, which represents the ratio in the number of atoms, using an inherent sensitivity correction value of the equipment. It is noted that the x-ray photoelectron spectroscopy equipment used for the Examples given herein was ESCA-1600, manufactured by Ulvac-Phi, Incorporated, and the sensitivity correction value inherent in this equipment was 2.33.

<Running stability>

20 **[0101]** For model evaluation for moldability, the running stability is determined as follows. A running stability evaluation unit is constructed on which five V-groove rollers with a diameter of 50 mm, a groove width of 10 mm, and a groove depth of 10 mm are fixed along a straight line at intervals of 300 mm. A carbon fiber bundle being evaluated, which is free of a sizing agent, is set in a zigzag pattern so that its top surface, bottom surface, top surface, bottom surface, and top surface are in contact with the V-groove rollers of the running stability evaluation unit, and moved for 30 minutes at a linear speed of 10 m/min while applying a tension of 1 kg using a dancer weight. Then, the carbon fiber bundle is removed and the condition of the five V-groove rollers is visually inspected and ranked as follows.

30 A: The rollers are free of carbon fibers adhered thereon. In addition, a test piece ranked as A is further subjected to the running test for additional 150 minutes and ranked as AA if the rollers are still free of carbon fibers adhered thereon.

B: A few carbon fibers are found attached on the rollers (attached on one or two of the five rollers).

C: Carbon fibers are found attached on the rollers (attached on three or four of the five rollers).

D: Many carbon fibers are found attached on the rollers (attached on all of the five rollers).

35 Examples

[0102] The present invention will now be illustrated in detail with reference to Examples, but it should be understood that the invention is not construed as being limited thereto.

40 **[0103]** In the Examples 1 to 11 and Comparative examples 1 to 16 given below, the procedure described in the following Comprehensive example is carried out under the conditions specified in Table 1 or Table 2.

[Comprehensive example]

45 **[0104]** A monomer compound consisting of acrylonitrile and itaconic acid was polymerized by the solution polymerization method using dimethyl sulfoxide as solvent to prepare a spinning dope solution containing a polyacrylonitrile copolymer. A coagulated fiber was produced through a dry-jet wet spinning process in which the resulting spinning dope solution was first filtered, discharged into air through a spinneret, and introduced into a coagulation bath containing an aqueous solution of dimethyl sulfoxide. Then, the coagulated fiber was rinsed, stretched in a hot water bath at 90°C to an underwater stretching ratio of 3, treated with an oil agent, dried using a roller heated at a temperature of 160°C , and subjected to pressurized steam stretching to a stretching ratio of 4 to prepare a precursor fiber bundle for carbon fiber having a single-fiber fineness of 1.1 dtex. Subsequently, four of such precursor fiber bundles for carbon fiber were combined to form a bundle containing 12,000 single fibers and heat-treated at a stretching ratio of 1 in an air atmosphere in an oven at 240°C to 280°C , there by converting it into a stabilized fiber bundle.

55 [Example 1]

[0105] After obtaining a stabilized fiber bundle by the procedure described in Comprehensive example, the resulting

EP 3 808 880 A1

5 stabilized fiber bundle was twisted to 75 turns/m and subjected to pre-carbonization treatment at a stretching ratio of 0.97 in a nitrogen atmosphere at a temperature of 300°C to 800°C to provide a pre-carbonized fiber bundle. Then, thus pre-carbonized fiber bundle was subjected to carbonization treatment under the conditions shown in Table 1 and electro-
10 lytic surface treatment with a quantity of electricity of 30 coulombs per gram of the carbon fiber bundle using an aqueous sulfuric acid solution as electrolyte to provide a carbon fiber bundle having a surface oxygen concentration (O/C) of 0.09. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Example 2]

15 **[0106]** Except that the twist count was 50 turns/m and that the tension in the carbonization treatment step was 5.2 mN/dtex, the same procedure as in Example 1 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Example 3]

20 **[0107]** Except that the tension in the carbonization treatment step was 10.2 mN/dtex, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Example 4]

25 **[0108]** Except that the twist count was 20 turns/m and that the tension in the carbonization treatment step was 10.3 mN/dtex, the same procedure as in Example 1 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

30 [Example 5]

35 **[0109]** Except that, unlike the Comprehensive example, eight precursor fiber bundles were combined to integrate 24,000 single fibers, the same procedure as in Example 3 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Example 6]

40 **[0110]** Except for performing carbonization treatment at or below a maximum temperature of 2,350°C under a tension of 6.5 mN/dtex in the carbonization treatment step, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was highly rated as A in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

45 [Example 7]

[0111] Except that the tension in the carbonization treatment step was 9.1 mN/dtex, the same procedure as in Example 6 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was highly rated as A in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

50 [Example 8]

55 **[0112]** Except that the tension in the carbonization treatment step was 11.6 mN/dtex, the same procedure as in Example 6 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was highly rated as A in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Example 9]

5 **[0113]** Except that the twist count was 20 turns/m and that the tension in the carbonization treatment step was 11.0 mN/dtex, the same procedure as in Example 5 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Example 10]

10 **[0114]** Except that the twist count was 5 turns/m, the same procedure as in Example 9 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was very highly rated as AA in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

15 [Example 11]

20 **[0115]** Except that, unlike the Comprehensive example, two precursor fiber bundles were combined to integrate 6,000 single fibers, the same procedure as in Example 3 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was highly rated as A in moldability. Evaluation results of the carbon fiber obtained are described in Table 1.

[Comparative Example 1]

25 **[0116]** Except that the twist count was 0 turn/m and that the tension in the carbonization treatment step was 5.3 mN/dtex, the same procedure as in Example 1 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the residual twist count was not within the range specified for the present invention, it was rated as B in moldability, indicating a deterioration compared with Example 1. Evaluation results of the carbon fiber obtained are described in Table 2.

30 [Comparative example 2]

35 **[0117]** Except that the twist count was 0 turn/m and that the tension and the maximum temperature in the carbonization treatment step were 5.3 mN/dtex and 1,400°C, respectively, the same procedure as in Example 3 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the residual twist count was not within the range specified for the present invention, it was rated as B in moldability, indicating a deterioration compared with Example 1. Evaluation results of the carbon fiber obtained are described in Table 2.

40 [Comparative example 3]

45 **[0118]** Except that the tension in the carbonization treatment step was 1.0 mN/dtex, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Although it was highly rated as A in moldability, the tension in the carbonization treatment step was not within the range specified for the present invention, and as a result, the carbon fiber prepared had a lower elastic modulus than in Example 1. Evaluation results of the carbon fiber obtained are described in Table 2.

[Comparative example 4]

50 **[0119]** Except that the precursor fiber bundle for carbon fiber used had a single-fiber fineness of 0.8 dtex and that the tension and the maximum temperature in the carbonization treatment step were 10.3 mN/dtex and 1,400°C, respectively, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the precursor fiber bundle for carbon fiber used had a small single-fiber fineness, it was rated as B in moldability, indicating a deterioration compared with Example 2. Evaluation results of the carbon fiber obtained are described in Table 2.

55 [Comparative example 5]

[0120] Except that the tension in the carbonization treatment step was 1.0 mN/dtex and that specimen was free of

twist, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was rated as B in moldability, indicating a small deterioration. Evaluation results of the carbon fiber bundle obtained are described in Table 2.

5 [Comparative example 6]

[0121] Except that the precursor fiber bundle for carbon fiber used had a single-fiber fineness of 0.8 dtex and that the tension and the maximum temperature in the carbonization treatment step were 10.3 mN/dtex and 1,900°C, respectively, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the residual twist count was not within the range specified for the present invention, it was rated as B in moldability, indicating a deterioration compared with Example 2. Evaluation results of the carbon fiber bundle obtained are described in Table 2.

15 [Comparative example 7]

[0122] Except that the tension in the carbonization treatment step was 1.6 mN/dtex, the same procedure as in Example 6 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. It was rated as B in moldability, indicating a small deterioration. Evaluation results of the carbon fiber obtained are described in Table 2.

20 [Comparative example 8]

[0123] Except that the twist count was 0 turns/m, the same procedure as in Example 3 was carried out to perform carbonization. The phenomenon of fracturing of the fiber being treated in the carbonization occurred so frequently that it was difficult to sample the carbon fiber bundle.

[Comparative example 9]

[0124] Except that the twist count was 0 turn/m, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. A certain degree of fuzz generation was seen in the carbonization step, but it was possible to sample the carbon fiber bundle. The carbon fiber bundle prepared suffered fuzz generation and was low in quality. Since the residual twist count was not within the range specified for the present invention, it was rated as B in moldability, indicating a deterioration compared with Example 2. Evaluation results are described in Table 2.

35 [Comparative example 10]

[0125] Except that the tension in the carbonization treatment step was 3.4 mN/dtex, the same procedure as in Comparative example 9 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Furthermore, since the residual twist count was not within the range specified for the present invention, it was rated as B in moldability, indicating a deterioration compared with Example 2. Evaluation results are described in Table 2.

45 [Comparative example 11]

[0126] Except that, unlike the Comprehensive example, two precursor fiber bundles were combined to integrate 6,000, that the twist count was 0 turn/m, and that the tension in the carbonization treatment step was 3.4 mN/dtex, the same procedure as in Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Since the residual twist count and the total fineness were not within the ranges specified for the present invention, it was rated as C in moldability, indicating a deterioration compared with Example 2. Evaluation results are described in Table 2.

55 [Comparative example 12]

[0127] Except that the twist count was 50 turn/m, the same procedure as Comparative example 11 was carried out to

produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Since the total fineness was not within the range specified for the present invention, it was rated as B in moldability, indicating a deterioration compared with Example 2. Evaluation results are described in Table 2.

[Comparative example 13]

[0128] Except that, unlike the Comprehensive example, the precursor fiber bundle had a single-fiber fineness of 0.8 dtex and that the tension in the carbonization treatment step was 3.4 mN/dtex, the same procedure as Example 2 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Since the precursor fiber bundle for carbon fiber used had a small single-fiber fineness, it was rated as B in moldability, indicating a deterioration compared with Example 2. Evaluation results are described in Table 2.

[Comparative example 14]

[0129] Except that the twist count was 0 turn/m, the same procedure as Comparative example 13 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Since the precursor fiber bundle for carbon fiber used had a small single-fiber fineness and the residual twist count was not within the range specified for the present invention, it was rated as D in moldability, indicating a lower stability compared with Example 2. Evaluation results are described in Table 2.

[Comparative example 15]

[0130] Except that, unlike the Comprehensive example, two precursor fiber bundles were combined to integrate 6,000 single fibers, the same procedure as Comparative example 13 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Since the precursor fiber bundle for carbon fiber used had a small single-fiber fineness and the total fineness was not within the range specified for the present invention, it was rated as C in moldability, indicating a deterioration compared with Example 2. Evaluation results are described in Table 2.

[Comparative example 16]

[0131] Except that the twist count was 0 turn/m, the same procedure as Comparative example 15 was carried out to produce a carbon fiber bundle. The processability in the carbonization step was high and the resulting carbon fiber bundle had good quality. Since the tension in the carbonization treatment step was not within the range specified for the present invention, the carbon fiber prepared had a lower elastic modulus than in Example 2. Since the precursor fiber bundle for carbon fiber used had a small single-fiber fineness and the residual twist count the total fineness was not within the range specified for the present invention, it was rated as D in moldability, indicating a lower stability compared with Example 2. Evaluation results are described in Table 2.

[Reference example 1]

[0132] Evaluation results of Torayca (registered trademark) T700S (manufactured by Toray Industries, Inc.) are described in Table 2. A sized specimen had a knot strength of 826 MPa. It was rated as B in moldability, indicating a small deterioration.

[Reference example 2]

[0133] Evaluation results of Torayca (registered trademark) M35J (manufactured by Toray Industries, Inc.) are described in Table 2.

[Reference example 3]

[0134] Evaluation results of Torayca (registered trademark) M40J (manufactured by Toray Industries, Inc.) are described in Table 2.

[Reference example 4]

[0135] Evaluation results of Torayca (registered trademark) M46J (manufactured by Toray Industries, Inc.) are described in Table 2.

[Reference example 5]

[0136] Evaluation results of Torayca (registered trademark) M40 (manufactured by Toray Industries, Inc.) are described in Table 2.

[Table 1-1]

| | precursor fiber | twisting | carbonization | | |
|------------|-----------------------|-------------|---------------------|---------|---------------------------------------|
| | single-fiber fineness | twist count | maximum temperature | tension | filament number in carbonization step |
| | dtex | turns/m | °C | mN/dtex | number |
| Example 1 | 1.1 | 75 | 1,900 | 6.1 | 12,000 |
| Example 2 | 1.1 | 50 | 1,900 | 5.2 | 12,000 |
| Example 3 | 1.1 | 50 | 1,900 | 10.2 | 12,000 |
| Example 4 | 1.1 | 20 | 1,900 | 10.3 | 12,000 |
| Example 5 | 1.1 | 50 | 1,900 | 10.2 | 24,000 |
| Example 6 | 1.1 | 50 | 2,350 | 6.5 | 12,000 |
| Example 7 | 1.1 | 50 | 2,350 | 9.1 | 12,000 |
| Example 8 | 1.1 | 50 | 2,350 | 11.6 | 12,000 |
| Example 9 | 1.1 | 20 | 1,900 | 11.0 | 24,000 |
| Example 10 | 1.1 | 5 | 1,900 | 11.0 | 24,000 |
| Example 11 | 1.1 | 50 | 1,900 | 10.2 | 6,000 |

[Table 1-2]

| carbon fiber | | | | | | | | | | | | | | Mold ability | | | | |
|-----------------------|-----------------|----------------|-----------------|------------------------|----------------------|------------------------------------|------------------------|---|-----------------------------------|--|---------------|-------------|------------------------------|--------------------|-------------|-------------|-------------|-------------------|
| single-fiber diameter | density | total fineness | strand strength | strand elastic modulus | residual twist count | twist angle of fiber surface layer | crystallite size L_c | orientation parameter of crystallites π_{002} | average crystallite size $L_c(s)$ | average orientation parameter of crystallites $\pi_{002}(s)$ | knot strength | formula (2) | single-fiber elastic modulus | loop fracture load | formula (1) | formula (3) | formula (4) | running stability |
| μm | g/cm^3 | g/km | GPa | GPa | turns/m | o | nm | % | nm | % | MPa | yes/no | GPa | N | yes/no | yes/no | yes/no | - |
| Example 1 | 1.72 | 888 | 4.1 | 367 | 73 | 10.5 | 2.8 | 85.2 | 2.8 | 85.5 | 343 | yes | 350 | 0.49 | yes | yes | yes | AA |
| Example 2 | 1.74 | 874 | 5.3 | 364 | 47 | 6.7 | 2.9 | 85.6 | 2.9 | 85.5 | 358 | yes | 345 | 0.52 | yes | yes | yes | AA |
| Example 3 | 1.74 | 850 | 4.3 | 392 | 47 | 6.6 | 2.9 | 87.2 | 2.9 | 87.1 | 343 | yes | 370 | 0.47 | yes | yes | yes | AA |
| Example 4 | 1.74 | 850 | 4.5 | 408 | 19 | 2.7 | 2.9 | 87.1 | 3.0 | 86.8 | 307 | yes | 400 | 0.47 | yes | yes | yes | AA |
| Example 5 | 1.73 | 1690 | 4.1 | 385 | 47 | 9.4 | 2.9 | 87.2 | 2.9 | 86.8 | 375 | yes | 370 | 0.46 | yes | yes | yes | AA |
| Example 6 | 1.91 | 761 | 4.0 | 480 | 47 | 6.0 | 4.6 | 88.2 | 4.5 | 88.4 | 186 | yes | 464 | 0.31 | yes | no | yes | A |
| Example 7 | 1.91 | 761 | 4.4 | 499 | 47 | 6.0 | 4.5 | 90.2 | 4.5 | 90.0 | 219 | yes | 470 | 0.30 | yes | no | yes | A |
| Example 8 | 1.84 | 755 | 4.3 | 493 | 47 | 6.1 | 4.5 | 90.4 | 4.5 | 90.3 | 156 | yes | 473 | 0.30 | yes | no | yes | A |
| Example 9 | 1.74 | 1700 | 4.5 | 400 | 18 | 3.6 | 2.9 | 87.3 | 2.9 | 87.0 | 370 | yes | 388 | 0.47 | yes | yes | yes | AA |
| Example 10 | 1.74 | 1700 | 4.8 | 405 | 4 | 0.8 | 2.9 | 87.5 | 2.9 | 87.1 | 380 | yes | 392 | 0.46 | yes | yes | yes | AA |

5
10
15
20
25
30
35
40
45
50
55

(continued)

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------|--|-----------------------|-------------------|-----|------|-----|------|-----|-----|-----|-----------------|------------------------|----------------|------------------------------------|---------------------|---|-----------------------------------|--|---------------|-------------|------------------------------|--------------------|-------------|-------------|-------------|--------------------|--------|--------|---|---|
| | | carbon fiber | | | | | | | | | | Mold ability | | | | | | | | | | | | | | | | | | |
| | | single-fiber diameter | g/cm ³ | 7.2 | 1.74 | 425 | g/km | 4.4 | GPa | 4.4 | strand strength | strand elastic modulus | residual count | twist angle of fiber surface layer | crystallite size LC | orientation parameter of crystallites π_{002} | average crystallite size $L_c(s)$ | average orientation parameter of crystallites $\pi_{002}(s)$ | knot strength | formula (2) | single-fiber elastic modulus | loop fracture load | formula (1) | formula (3) | formula (4) | run-ning stability | | | | |
| Example 11 | | μm | | 7.2 | 1.74 | 425 | g/km | 4.4 | GPa | 4.4 | 394 | turns/m | o | nm | 2.9 | 87.2 | nm | 2.9 | 87.1 | 343 | yes/no | GPa | N | 0.47 | yes/no | yes/no | yes/no | yes/no | - | A |

EP 3 808 880 A1

[Table 2-1]

| 5 | | precursor fiber | twisting | carbonization | | |
|----|------------------------|-----------------------|-------------|---------------------|---------|---------------------------------------|
| | | single-fiber fineness | twist count | maximum temperature | tension | filament number in carbonization step |
| | | dtex | turns/m | °C | mN/dtex | number |
| 10 | Comparative example 1 | 1.1 | 0 | 1,900 | 5.3 | 12,000 |
| | Comparative example 2 | 1.1 | 0 | 1,400 | 5.4 | 12,000 |
| 15 | Comparative example 3 | 1.1 | 50 | 1,900 | 1.0 | 12,000 |
| | Comparative example 4 | 0.8 | 50 | 1,400 | 10.3 | 12,000 |
| 20 | Comparative example 5 | 1.1 | 0 | 1,900 | 1.0 | 12,000 |
| | Comparative example 6 | 0.8 | 50 | 1,900 | 10.3 | 12,000 |
| 25 | Comparative example 7 | 1.1 | 50 | 2,350 | 1.6 | 12,000 |
| | Comparative example 8 | 1.1 | 0 | 1,900 | 10.2 | 12,000 |
| 30 | Comparative example 9 | 1.1 | 0 | 1,900 | 5.2 | 12,000 |
| | Comparative example 10 | 1.1 | 0 | 1,900 | 3.4 | 12,000 |
| 35 | Comparative example 11 | 1.1 | 0 | 1,900 | 3.4 | 6,000 |
| | Comparative example 12 | 1.1 | 50 | 1,900 | 3.4 | 6,000 |
| 40 | Comparative example 13 | 0.8 | 50 | 1,900 | 3.4 | 12,000 |
| | Comparative example 14 | 0.8 | 0 | 1,900 | 3.4 | 12,000 |
| 45 | Comparative example 15 | 0.8 | 50 | 1,900 | 3.4 | 6,000 |
| | Comparative example 16 | 0.8 | 0 | 1,900 | 3.4 | 6,000 |
| 50 | Reference example 1 | - | - | - | - | 12,000 |
| | Reference example 2 | - | - | - | - | 12,000 |
| | Reference example 3 | - | - | - | - | 12,000 |
| | Reference example 4 | - | - | - | - | 12,000 |
| 55 | Reference example 5 | - | - | - | - | 6,000 |

[Table 2-2]

| | carbon fiber | | | | | | | | | | | | | | moldabil- ity | | | | |
|---------------------------------|--------------------------------|------------------------|------------------------|--------------------|-----------------------------------|------------------------------|---|--------------------------------|---|--|--|----------------------|------------------|---|------------------|-------------------------------|------------------|------------------|------------------|
| | single- fiber di- ameter | Densi- ty | total fine- ness | strand strength | strand elastic modu- lus | residu- al twist count | twist angle of fiber sur- face layer | crystal- lite size L_c | orienta- tion pa- rameter of crys- tallites π_{002} | average crystal- lite size $L_c(s)$ | average orienta- tion pa- rameter of crys- tallites $\pi_{002}(s)$ | knot strengt h | formu- la (2) | single- fiber elastic modu- lus | | loop frac- ture load | formu- la (1) | formu- la (3) | formu- la (4) |
| Compara- tive exam- ple 1 | μm | g/cm^3 | g/km | GPa | GPa | turns/ m | $^\circ$ | nm | % | nm | % | MPa | yes/no | GPa | N | yes/no | yes/no | yes/no | - |
| | 7.4 | 1.72 | 888 | 4.3 | 348 | 0 | 0.0 | 2.8 | 85.3 | 2.8 | 85.6 | 340 | no | 335 | 0.45 | no | yes | yes | B |
| Compara- tive exam- ple 2 | 7.4 | 1.79 | 924 | 4.6 | 314 | 0 | 0.0 | 2.0 | 82.6 | 2.0 | 82.3 | 402 | no | 301 | 0.50 | no | yes | yes | B |
| Compara- tive exam- ple 3 | 7.5 | 1.70 | 901 | 4.3 | 294 | 47 | 6.9 | 2.8 | 82.5 | 2.8 | 82.7 | 360 | no | 287 | 0.46 | no | no | no | A |
| Compara- tive exam- ple 4 | 5.3 | 1.81 | 479 | 5.3 | 361 | 47 | 4.9 | 2.1 | 85.1 | 2.1 | 85.5 | 391 | yes | 355 | 0.33 | no | yes | yes | B |
| Compara- tive exam- ple 5 | 7.5 | 1.71 | 914 | 4.3 | 296 | 0 | 0.0 | 2.7 | 82.6 | 2.7 | 82.3 | 323 | no | 282 | 0.51 | no | no | no | B |
| Compara- tive exam- ple 6 | 5.3 | 1.81 | 475 | 5.0 | 391 | 47 | 4.9 | 2.9 | 87.2 | 2.9 | 86.7 | 287 | yes | 378 | 0.28 | no | yes | yes | B |
| Compara- tive exam- ple 7 | 6.8 | 1.90 | 828 | 3.3 | 412 | 47 | 6.3 | 4.6 | 86.9 | 4.5 | 86.3 | 219 | no | 393 | 0.32 | no | no | no | B |

5
10
15
20
25
30
35
40
45
50
55

(continued)

| | carbon fiber | | | | | | | | | | | | | | moldabil- ity | | | | |
|----------------------------------|--------------------------------|--------------|------------------------|--------------------|-----------------------------------|------------------------------|---|--------------------------------|--|---|---|----------------------|------------------|---|------------------|-------------------------------|------------------|------------------|------------------|
| | single- fiber di- ameter | Densi- ty | total fine- ness | strand strength | strand elastic modu- lus | residu- al twist count | twist angle of fiber sur- face layer | crystal- lite size L_c | orienta- tion pa- rameter of crys- tallites π 002 | average crystal- lite size L_c (s) | average orienta- tion pa- rameter of crys- tallites π_{002} (s) | knot strengt h | formu- la (2) | single- fiber elastic modu- lus | | loop frac- ture load | formu- la (1) | formu- la (3) | formu- la (4) |
| Compara- tive exam- ple 8 | | | | | | turns/ m | ° | nm | % | nm | % | MPa | yes/no | GPa | N | yes/no | yes/no | yes/no | - |
| Compara- tive exam- ple 9 | 7.4 | 1.74 | 898 | 4.6 | 350 | 0 | 0.0 | 2.8 | 85.2 | 2.8 | 85.4 | 343 | no | 340 | 0.44 | no | yes | yes | B |
| Compara- tive exam- ple 10 | 7.4 | 1.74 | 898 | 4.7 | 340 | 0 | 0.0 | 2.9 | 84.0 | 2.9 | 83.9 | 355 | no | 325 | 0.46 | no | no | no | B |
| Compara- tive exam- ple 11 | 7.4 | 1.74 | 449 | 4.8 | 335 | 0 | 0.0 | 2.8 | 84.1 | 2.8 | 84.2 | 350 | no | 320 | 0.47 | no | no | yes | C |
| Compara- tive exam- ple 12 | 7.4 | 1.74 | 449 | 4.5 | 339 | 47 | 4.8 | 2.9 | 84.2 | 2.9 | 83.9 | 352 | no | 322 | 0.47 | no | no | no | B |
| Compara- tive exam- ple 13 | 5.4 | 1.80 | 495 | 5.0 | 342 | 47 | 5.0 | 2.9 | 83.9 | 2.9 | 84.1 | 325 | no | 324 | 0.28 | no | no | yes | B |
| Compara- tive exam- ple 14 | 5.4 | 1.80 | 495 | 5.0 | 340 | 0 | 0.0 | 2.9 | 84.1 | 2.9 | 84.2 | 321 | no | 325 | 0.28 | no | no | no | D |

Sampling of carbon fiber is difficult.

(continued)

| | carbon fiber | | | | | | | | | | | | | | | modal- bilit- ity | | | | | | |
|----|-----------------------------------|--------------|------------------------|--------------------|-----------------------------------|------------------------------|---|---|--|--|---|------------------|------------------|---|-------------------------------|-------------------------|------------------|------------------|--|--|--|---|
| | single- fiber di- ameter | Densi- ty | total fine- ness | strand strength | strand elastic modu- lus | residu- al twist count | twist angle of fiber sur- face layer | crystal- lite size L _c | orienta- tion pa- rameter of crys- tallites π 002 | average crystal- lite size L _c (s) | average orienta- tion pa- rameter of crys- tallites π_{002} (s) | knot strength | formu- la (2) | single- fiber elastic modu- lus | loop frac- ture load | formu- la (1) | formu- la (3) | formu- la (4) | | | | |
| 5 | | | | | | | | | | | | | | | | | | | | | | |
| 10 | | | | | | | | | | | | | | | | | | | | | | |
| 15 | | | | | | | | | | | | | | | | | | | | | | |
| 20 | | | | | | | | | | | | | | | | | | | | | | |
| 25 | | | | | | | | | | | | | | | | | | | | | | |
| 30 | | | | | | | | | | | | | | | | | | | | | | |
| 35 | | | | | | | | | | | | | | | | | | | | | | |
| 40 | | | | | | | | | | | | | | | | | | | | | | |
| 45 | | | | | | | | | | | | | | | | | | | | | | |
| 50 | | | | | | | | | | | | | | | | | | | | | | |
| 55 | | | | | | | | | | | | | | | | | | | | | | |
| | Compara- tive example 15 | 1.80 | 247 | 4.9 | 337 | 47 | 3.5 | 2.9 | 83.9 | 2.9 | 83.9 | 320 | no | 322 | 0.27 | no | no | no | | | | C |
| | Compara- tive exam- ple 16 | 1.80 | 247 | 4.9 | 333 | 0 | 0.0 | 2.9 | 83.9 | 2.9 | 84.0 | 323 | no | 323 | 0.27 | no | no | no | | | | D |
| | Reference example 1 | 1.80 | 831 | 4.9 | 230 | 0 | - | - | - | 1.7 | - | 262 | no | 232 | 0.43 | no | - | - | | | | B |
| | Reference example 2 | 1.75 | 446 | 4.7 | 343 | 0 | - | - | - | 3.3 | - | 313 | no | 333 | 0.28 | no | - | - | | | | C |
| | Reference example 3 | 1.75 | 446 | 4.4 | 377 | 0 | - | - | - | 3.7 | - | 127 | no | 350 | 0.24 | no | - | - | | | | C |
| | Reference example 4 | 1.84 | 451 | 4.2 | 436 | 0 | - | - | - | 4.9 | - | 98 | no | 413 | 0.25 | no | - | - | | | | C |
| | Reference example 5 | 1.77 | 363 | 3.0 | 387 | 0 | - | - | - | - | - | 8 | no | 375 | 0.18 | no | - | - | | | | C |

INDUSTRIAL APPLICABILITY

[0137] The present invention relates to a carbon fiber that has both a high tensile modulus and a high moldability in composite production and easily maintains a required fiber length even when used in the form of discontinuous fibers, also relates to a method for the production thereof. With such good features, carbon fiber bundles produced according to the present invention can be used suitably for manufacturing members of aircraft, automobiles, ships, etc., and general industrial articles including sporting goods such as golf shafts and fishing rods.

Claims

1. A carbon fiber having a strand elastic modulus of 360 GPa or more, a strand strength of 3.5 GPa or more, and a single-fiber diameter of 6.0 μm or more, and further satisfying either the requirement (a) or (b) specified below:

(a) when one end is fixed end and the other end being free end which is capable of rotation about the axis of the fiber bundle, the residual twist count is 2 turns/m or more, and

(b) the total fineness, which is the product of the single-fiber fineness (g/km) and the filament number (number) of the carbon fiber, is 740 g/km or more.

2. A carbon fiber as set forth in claim 1, meeting the relationship represented by formula (1), wherein E_s (GPa) is the single-fiber elastic modulus and A (N) is the loop fracture load:

$$A \geq -0.0017 \times E_s + 1.02 \quad \text{formula (1).}$$

3. A carbon fiber as set forth in either claim 1 or 2, having a single-fiber diameter of 6.0 μm or more, satisfying the relationship represented by formula (2) wherein E (GPa) is the strand elastic modulus and B (MPa) is the knot strength determined under conditions where the heat loss rate is 0.15% or less at 450°C, and having a twist count of 20 to 80 turns/m:

$$B \geq 6.7 \times 10^9 \times E^{-2.85} \quad \text{formula (2).}$$

4. A carbon fiber as set forth in any one of claims 1 to 3, wherein the total fineness is 850 g/km.

5. A carbon fiber as set forth in any one of claims 1 to 4, wherein the strand elastic modulus is 440 GPa or more.

6. A carbon fiber as set forth in any one of claims 1 to 5, wherein the twist angle of the carbon fiber bundle surface layer is 2.0° to 30.5°.

7. A carbon fiber as set forth in claim 6, wherein the twist angle of the carbon fiber bundle surface layer is 4.8° to 10.0°.

8. A carbon fiber as set forth in any one of claims 1 to 7, wherein the single-fiber diameter is 6.5 μm or more.

9. A carbon fiber as set forth in any one of claims 1 to 8, wherein single-fiber diameter is 7.4 μm or less.

10. A carbon fiber as set forth in any one of claims 1 to 9, wherein the crystallite size L_c (nm) and the orientation parameter of crystallites π_{002} (%) satisfy the relationship represented by formula (3):

$$\pi_{002} \geq 4.0 \times L_c + 73.2 \quad \text{formula (3).}$$

11. A carbon fiber as set forth in any one of claims 1 to 10, wherein the crystallite size L_c is 2.2 to 3.5 nm.

12. A carbon fiber as set forth in any one of claims 1 to 11, wherein the strand elastic modulus E (GPa) and the crystallite size L_c (nm) satisfy the relationship represented by formula (4):

$$E \times Lc^{-0.5} \geq 200 \text{ (GPa/nm}^{0.5}) \quad \text{formula (4).}$$

5 13. A carbon fiber as set forth in any one of claims 1 to 12, wherein the surface oxygen concentration O/C is 0.05 to 0.50.

14. A carbon fiber bundle as set forth in any one of claims 1 to 13, wherein the filament number is 10,000 or more.

10 15. A carbon fiber meeting the relationship represented by formula (1) wherein E_s (GPa) is the single-fiber elastic modulus and A (N) is the loop fracture load:

$$A \geq -0.0017 \times E_s + 1.02 \quad \text{formula (1).}$$

15 16. A carbon fiber having a single-fiber diameter of 6.0 μm or more, satisfying the relationship represented by formula (2) wherein E (GPa) is the strand elastic modulus and B (MPa) is the knot strength determined under conditions where the heat loss rate is 0.15% or less at 450°C, and having a twist count of 5 to 80 turns/m:

$$B \geq 6.7 \times 10^9 \times E^{-2.85} \quad \text{formula (2).}$$

20 17. A carbon fiber as set forth in either claim 15 or 16, wherein either the single-fiber elastic modulus or the strand elastic modulus is 360 GPa or more.

25 18. A method for producing a carbon fiber comprising a step in which a precursor fiber bundle for carbon fiber is subjected to stabilization treatment in an air atmosphere in the temperature range of 200°C to 300°C, a step for pre-carbonization in which the resulting stabilized fiber bundle is heat-treated in an inert atmosphere at or below a maximum temperature of 500°C to 1,000°C until the density reaches 1.5 to 1.8 g/cm³, and a step for carbonization in which the resulting pre-carbonized fiber bundle is heat-treated in an inert atmosphere, the precursor fiber bundle for carbon fiber having a single-fiber fineness of 0.9 dtex or more, having a tension controlled at 5 mN/dtex or more during the carbonization treatment, meeting either the following requirement (c) or (d), and having a strand elastic modulus of 360 GPa or more:

30 (c) the fiber bundle to be subjected to the carbonization treatment has a twist count of 2 turns/m or more, and
 (d) the total fineness, which is the product of the single fiber fineness (g/km) and the filament number (number),
 35 of the resulting carbon fiber is 740 g/km or more.

19. A method for producing a carbon fiber as set forth in claim 18, wherein the fiber bundle to be subjected to carbonization treatment has a twist count of 16 turns/m or more.

40 20. A method for producing a carbon fiber as set forth in either claim 18 or 19, wherein the maximum temperature in the carbonization treatment step is 1,500°C or more.

21. A method for producing a carbon fiber as set forth in claim 20, wherein the maximum temperature in the carbonization treatment step is 2,300°C or more.

45 22. A method for producing a carbon fiber as set forth in any one of claims 18 to 21, wherein electrolytic surface treatment with an amount of current of 2 to 100 c/g is performed after the carbonization treatment step.

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/023851

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. D01F9/22 (2006.01) i, D01F6/18 (2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. D01F9/22, D01F6/18

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

| | |
|--|-----------|
| Published examined utility model applications of Japan | 1922-1996 |
| Published unexamined utility model applications of Japan | 1971-2019 |
| Registered utility model specifications of Japan | 1996-2019 |
| Published registered utility model applications of Japan | 1994-2019 |

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|--|
| X A | JP 2002-327374 A (TORAY INDUSTRIES, INC.) 15 November 2002, example 8, paragraphs [0064], [0076], claims (Family: none) | 1, 4-5, 8-9, 13-14 2-3, 6-7, 10-12, 15-22 |
| A | WO 2010/084856 A1 (TEIJIN LTD.) 29 July 2010, example 1 & TW 201042105 A | 1-22 |
| A | JP 51-105419 A (MORGANITE MODMOR LTD.) 18 September 1976, examples paragraphs [0001]-[0003] & US 4051659 A (example stages I-III) & GB 1498721 A & DE 2606290 A1 & FR 2300826 A | 1-22 |
| A | JP 11-269727 A (TORAY INDUSTRIES, INC.) 05 October 1999, claims (Family: none) | 1-22 |

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

20 August 2019 (20.08.2019)

Date of mailing of the international search report

27 August 2019 (27.08.2019)

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2008047745 A [0014]
- JP 2009256833 A [0014]
- WO 2008063886 A [0014]
- JP 2001049536 A [0014]
- JP HE110195718 B [0014]
- JP 2000160436 A [0014]
- JP SHO47026964 B [0014]
- JP SHO56091015 B [0014]
- JP 2002001725 A [0014]
- JP 2014141761 A [0014]
- WO 2013157613 A [0014]
- WO 2013157612 A [0014]