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(54) **CARBON FIBER BUNDLE THAT DEVELOPS HIGH MECHANICAL PERFORMANCE**

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(57) **ABSTRACT**

Provided is a carbon fiber bundle for obtaining a fiber-reinforced resin having high mechanical characteristics. A carbon fiber bundle formed of single carbon fibers, each of which has no uneven surface structure of 0.6 μm or more in length extending in the longitudinal direction of the single fiber; which has an uneven structure having a difference in height (Rp−v) of 5 to 25 nm between the highest portion and the lowest portion of the surface of the single fiber and having an average roughness Ra of 2 to 6 nm; and which has a ratio of the major axis to the minor axis (major axis/minor axis) of a cross-section of the single fiber of 1.00 to 1.01, wherein a mass of the single fiber per unit length falls within the range of 0.030 to 0.042 mg/m; a strand strength is 5900 MPa or more; a strand elastic modulus measured by the ASTM method is 250 to 380 GPa; and a knot tenacity is 900 N/mm^2 or more.

CARBON FIBER BUNDLE THAT DEVELOPS HIGH MECHANICAL PERFORMANCE

TECHNICAL FIELD

[0001] The present invention relates to a carbon fiber bundle that has excellent mechanical characteristics and that is particularly used for obtaining a fiber-reinforced resin using a high-tenacity heat resistant resin as a matrix for use in the construction of airplanes.

BACKGROUND ART

[0002] Conventionally, in order to improve the mechanical characteristics of resin-base molded products, a resin has been commonly used in combination with a fiber serving as a reinforcement material. In particular, a composite molding material formed of a carbon fiber that is excellent in specific strength and specific elasticity in combination with a high-performance resin develops extremely high mechanical characteristics. Because of this, such a molding material has been willingly used as a constructional material for airplanes, high speed moving bodies, etc. Furthermore, there is a demand for developing a material that is stronger and that has higher rigidity as well as having excellent specific strength and specific rigidity. Given these circumstances, the desire is for further improvement of the performance of carbon fiber, such as improved strength and elastic modulus.

[0003] For example, Patent Literature 1 proposes a method of drawing a coagulated fiber that still contains a solvent in a solvent-containing drawing bath, thereby improving uniformity in structure and orientation, in order to obtain an acrylic fiber bundle used as a precursor of a carbon-fiber by a dry-wet spinning method. Drawing a coagulated fiber in a bath containing a solvent is a method commonly known as a solvent drawing technique that enables a stable drawing process by using solvent plasticization. Accordingly, this method is considered as an extremely excellent technique for obtaining a fiber that has high uniformity in structure and orientation. However, if a fiber bundle that is in a swollen state due to the presence of a solvent is drawn, the solvent within a filament is rapidly squeezed out from the filament simultaneously upon drawing. The resultant structure of the filament tends to be less dense and thus a desired filament that has a dense structure cannot be obtained.

[0004] Furthermore, Patent Literature 2, which pays attention to fine pores distributed in a coagulated fiber, proposes a technique for obtaining a precursor fiber in which excellent strength is developed by dry-densification of a coagulated fiber that has a high-dense structure. The fine pore distribution, which is obtained by a mercury press-in method, reflects the bulk state from the surface layer to the interior of the filament. This is an extremely excellent method for evaluating the overall density of a fiber structure. From the precursor fiber bundle that has at least a certain level density as a whole, a very strong carbon fiber can be obtained in which defect point formation is suppressed. However, observation of fractures in the carbon fiber shows that fractures have originated from near the surface layer at an extremely high ratio. This means that a defective point is present near the surface layer. In other words, this technique is insufficient for manufacturing a precursor fiber bundle that is excellent in density near the surface layer.

[0005] Patent Literature 3 proposes a method for manufacturing an acrylonitrile-based precursor fiber bundle that is not only high in whole density but that is also extremely high in surface density. Furthermore, Patent Literature 4 proposes, taking into consideration that an oil solution enters the surface-layer portion of a fiber and inhibits densification, a technique for suppressing permeation of an oil solution by focusing on microscopic voids of the surface-layer portion. However, a technique for suppressing the entry of an oil solution and a technique for suppressing defective point formation are both difficult to put into practical use since very complicated steps are required. Therefore, in the techniques discussed above, the effect of stably suppressing the entry of an oil solution into the surface layer portion is insufficient and the effect of reinforcing a carbon fiber is still far from a sufficient level.

CITATION LIST

Patent Literatures

[0006] Patent Literature 1: JP05-5224A
[0007] Patent Literature 2: JP04-91230A
[0008] Patent Literature 3: JP06-15722A
[0009] Patent Literature 4: JP11-124744A

SUMMARY OF INVENTION

Technical Problem

[0010] An object of the present invention is to provide a carbon fiber bundle for obtaining a fiber-reinforced resin that has high mechanical characteristics.

Solution to Problem

[0011] The object is attained by the invention set forth below.

[0012] The present invention is directed to a carbon fiber bundle formed of single carbon fibers, each of which has no surface uneven structure of 0.6 μm or more in length extending in the longitudinal direction of the single fiber; which has an uneven structure having a difference in height (Rp−v) of 5 to 25 nm between the highest portion and the lowest portion of the surface of the single fiber and an average roughness Ra of 2 to 6 nm, and which has a ratio of the major axis to the minor axis (major axis/minor axis) of a cross-section of the single fiber of 1.00 to 1.01, in which a mass of the single fiber per unit length falls within the range of 0.030 to 0.042 mg/m, a strand strength is 5900 MPa or more, a strand elastic modulus measured by the ASTM method is 250 to 380 GPa and a knot tenacity is 900 N/mm^2 or more.

[0013] Note that the knot tenacity can be obtained by dividing the tensile breaking stress of a knotted carbon fiber bundle by the cross-sectional area of the fiber bundle (mass and density per unit length).

Advantageous Effects of Invention

[0014] According to the carbon fiber bundle of the present invention, it is possible to provide a fiber-reinforced resin that has high mechanical characteristics.

[0015] Furthermore, a carbon fiber bundle that has even better performance is obtained by acquiring "surface energy of surface formed by fracture" such that it reaches 30N/m or more.

[0016] Moreover, a carbon-fiber composite material that has extremely high mechanical performance can be obtained by forming a carbon fiber bundle which has an ipa value of 0.05 to 0.25 $\mu A/cm^2$ that is obtained by an electrochemical

measuring method (cyclic voltammetry), and in which the amount of an oxygen-containing functional group (O1S/C1S) in a carbon fiber surface, that is obtained by X-ray photoelectron spectroscopy, is within the range of 0.05 to 0.10.

DESCRIPTION OF EMBODIMENTS

[0017] The uneven surface structure present on the surface of a carbon fiber and extending in the longitudinal direction thereof and a sizing agent attached onto the surface play very important roles in developing mechanical characteristics of a fiber-reinforced resin material that uses the carbon fiber as a reinforcement material. This is because the uneven surface structure and the sizing agent attached onto the surface are directly involved in formation of the interfacial phase between a carbon fiber and a resin as well as characteristics thereof. The mechanical performance of the fiber-reinforced resin material is influenced by the performance of each of the three constituent factors, i.e., the fiber, the matrix resin and the interfacial phase. Even if only one of the three factors is unsatisfactory, the fiber-reinforced resin material cannot develop excellent mechanical performance.

(Uneven Surface Structure of a Single Fiber Extending in the Longitudinal Direction)

[0018] A carbon fiber obtained by a general manufacturing method for a carbon fiber bundle generally has an uneven surface structure that is formed almost parallel to the fiber-axis direction. The uneven structure has an undulation structure that is almost parallel to the fiber axis and that extends in the fiber axis. The depth of the uneven structure is usually about 50 nm to several hundreds of nm and the length thereof is usually about 0.6 μm to several μm and sometimes, several tens of μm. Such an uneven surface structure is usually called as surface wrinkle.

[0019] The carbon fiber bundle of the present invention does not have an uneven surface structure that has a length of 0.6 μm or more and that extends in the longitudinal direction of a single fiber.

[0020] In contrast, the carbon fiber bundle of the present invention has an uneven structure that is smaller than the uneven structure mentioned above on the surface of a single fiber. The depth of the uneven surface structure present on a single carbon fiber is defined by the difference in height (Rp−v) between the highest portion and the lowest portion on the surface of a fiber and the average roughness Ra, in an area range surrounded by a length of 1.0 μm in the fiber-circumference direction and a length 1.0 μm in the fiber-axis direction. The (Rp−v) and Ra can be obtained by scanning the surface of a single fiber by use of a scanning atomic force microscope (AFM). It is desirable that the difference in height (Rp−v) be 5 to 25 nm and that the average roughness Ra be 2 to 6 nm. It is more preferable that the difference in height (Rp−v) be 5 to 18 nm and that Ra be 2 to 5 nm.

[0021] In the present invention, each of the single fibers that constitutes a carbon fiber has no uneven surface structure that has a length of 0.6 μm or more and that extends in the longitudinal direction of the fiber, on the surface of a single fiber. In the interfacial phase of a composite material, stress tends to be concentrated on such a large uneven surface structure. In addition, the fracture toughness of carbon fiber tissue around such an uneven structure is low. Accordingly, in the uneven surface structure of this size, interfacial failure tends to originate from a point near the uneven structure even if the level of stress applied to a composite material is not very large. As a result, mechanical performance of the composite material significantly decreases.

[0022] A more specific embodiment of the uneven surface structure of each of the single fibers constituting a carbon fiber bundle of the present invention is as follows.

[0023] Usually, carbon-fiber surface has an uneven structure of 0.6 μm or more in length called a wrinkle structure, that has an assembly of several fibrils as a unit and that extends in the longitudinal direction of the fiber, and an uneven microscopic structure that is smaller than the uneven structure called a wrinkle structure and that is present in each fibril body itself.

[0024] On the contrary, on the surface of each of the single fibers constituting a carbon fiber bundle of the present invention, an uneven structure that has a length of 0.6 μm or more and that extends in the longitudinal direction of a fiber is not present but only an uneven microscopic structure that is smaller than the uneven structure and that is present in each fibril body itself is present. Furthermore, such an uneven microscopic structure has a length of 300 nm or less. The uneven structure is defined by (Rp−v) and Ra as mentioned above. To be specific, the uneven structure is an undulation structure having a difference in height (Rp−v) of 5 to 25 nm and an average roughness Ra of 2 to 6 nm, which are present in an area range surrounded by a length (1.0 μm) in the fiber-circumference direction of a single-fiber surface and a length (1.0 μm) in the fiber-axis direction. Preferably, (Rp−v) is 5 to 18 nm and Ra is 2 to 5 nm. The direction of the uneven microscopic structure is not particularly limited and may be parallel or perpendicular to the fiber-axis direction or may be present at an angle with the fiber-axis direction.

(Cross-Section of Single Fiber)

[0025] Furthermore, the ratio of the major axis and the minor axis (major axis/minor axis) of a single fiber cross-section is 1.00 to 1.01. This means that the single fiber must have a complete circular or nearly complete circular cross-section. This is because if the cross-section is a complete circle, the portion near the fiber surface has excellent structural uniformity, with the result that concentration of stress can be reduced. The ratio is preferably 1.00 to 1.005. Furthermore, for the same reason, the mass of the single fiber per unit length is 0.030 to 0.042 mg/m. If the mass of the single fiber per unit length (single fiber weight per unit area) is low, the fiber diameter is small, and structural irregularity along the cross-section is small. This means that mechanical performance in the direction perpendicular to the fiber axis is high. Accordingly, in a composite material, tolerance to stress applied in the direction perpendicular to the fiber axis is improved and the mechanical performance of a composite material can be enhanced.

(Carbon Fiber Bundle)

[0026] In the present invention, to obtain a fiber-reinforced resin having excellent mechanical characteristics, the strand strength of a carbon fiber bundle must be 5900 MPa or more. The strand strength of a carbon fiber bundle is preferably 6000 MPa or more and more preferably 6100 MPa or more. The higher the strand strength, the better; however, taken into consideration the balance between the strand strength and the compressive strength of a composite material, 10000 MPa is

sufficient. Furthermore, in the present invention, to obtain a fiber-reinforced resin having excellent mechanical characteristics, the strand elastic modulus of a carbon fiber bundle must be 250 to 380 GPa, which are values measured by the ASTM method. If the elastic modulus is less than 250 GPa, the elastic modulus of a carbon fiber bundle will be insufficient and sufficient mechanical characteristics cannot develop. In contrast, if the elastic modulus exceeds 380 GPa, the graphite crystal size of the surface and interior of a carbon fiber will increase. In accordance with this, the strength along the cross-section of the fiber and the compressive strength in the fiber-axis direction decrease and performance balance between tension and compression of a composite material cannot be maintained. As a result, excellent composite material cannot be obtained. In addition, inactivation of the surface proceeds as the graphite crystal size increases, and the adhesiveness with a matrix resin decreases. As a result, mechanical performance such as tensile strength of the composite material in the direction of 90°, interlayer shearing strength, in-plane shearing strength and 0° compressive strength significantly decreases.

[0027] Furthermore, in the present invention, it is important that the knot tenacity, which is obtained by dividing the tensile stress at break of a knotted carbon fiber bundle by the cross-sectional area of the fiber bundle (mass and density per unit length), is 900 N/mm^2 or more. More preferably, the knot tenacity is 1000 N/mm^2 or more and further preferably, 1100 N/mm^2 or more. The knot tenacity serves as an index that reflects the mechanical performance of a fiber bundle except in the fiber-axis direction. In particular, the performance in the direction perpendicular to the fiber axis can be simply checked by the knot tenacity. In the composite material, since a material is often formed by pseudo-isotropic lamination, a complicated stress field is formed. At this time, other than tension and compression stress in the fiber-axis direction, stress is also generated in the fiber-axis direction. Furthermore, if a relatively high-speed strain is applied, as is in an impact test, the state of the stress that is generated within the composite material is considerably complicated and the strength in the direction that is different from the strength in the fiber-axis direction becomes important. Accordingly, if the knot tenacity is less than 900 N/mm^2, sufficient mechanical performance does not develop in a pseudo-isotropic material. On the other hand, if the knot tenacity exceeds 3000 N/mm^2, the degree of orientation in the fiber-axis direction must be reduced. Accordingly, the knot strength should be controlled to be 3000 N/mm^2 or less.

[0028] Furthermore, in the carbon fiber bundle of the present invention, a "surface energy of surface formed by fracture" is preferably 30 N/m or more. The surface energy of surface formed by fracture is obtained by forming a hemispherical defect having a predetermined size by a laser on the surface of a single fiber, and by breaking the fiber at the hemispherical defective site in a tensile test and by calculating from the breaking strength of the fiber and the size of the hemispherical defect in accordance with the following Griffith Equation (1).

$$\sigma=(2E/\pi C)^{1/2}\times(\text{surface energy of surface formed by fracture})^{1/2} \quad (1)$$

Here, "σ" is the breaking strength; "E" is the ultrasonic elastic modulus of a carbon fiber bundle; and "C" is the size of a hemispherical defect. The "surface energy of surface formed by fracture" is more preferably, 31 N/m or more and further preferably 32 N/m or more.

[0029] The surface energy of surface formed by fracture herein is used as a break-proof index of a carbon fiber for representing substrate strength. The carbon fiber is a material showing brittle fracture and the tensile strength is controlled by the defective point. If carbon fibers have the same defective points, the breaking strength increases as the substrate strength increases. Furthermore, a matrix resin for a high-performance composite material often has high adhesiveness with a carbon fiber, with the result that the critical fiber length, which serves as an index for stress transfer, diminishes. As a result, the strength in a further shorter length is reflected in the strength of the composite material. Thus, the substrate strength is conceivably an important index. In contrast, if the surface energy produced by breaking exceeds 50 N/m, it is necessary to reduce the degree of orientation in the fiber-axis direction. Accordingly, the surface energy produced by breaking should be 50 N/m or less.

[0030] In the present invention, the ipa value obtained by an electrochemical measuring method (cyclic voltammetry) is preferably 0.05 to 0.25 $\mu A/cm^2$. The ipa value is influenced by the number of oxygen-containing functional groups of a carbon fiber, surface roughness involved in formation of an electric double layer and the microscopic graphite structure of a carbon fiber surface. In particular, a carbon fiber whose surface is largely etched and a carbon fiber that has an intercalation compound which is formed by inserting an anion between layers of a graphite crystal have a large ipa value. In developing composite material that has excellent mechanical performance, the interface between a carbon fiber and a resin is important. In particular, a carbon fiber that has a surface in which an appropriate oxygen-containing functional group is present and in which a small electric double layer is formed, is found to form the most appropriate interface. If an ipa value is 0.05 $\mu A/cm^2$ or more, it indicates that the surface has a sufficient number of oxygen-containing functional groups, and it exhibits sufficient adhesiveness to an interface. In contrast, if an ipa value is 0.25 $\mu A/cm^2$ or less, the surface is not excessively etched and an intercalation compound is not formed. Such a surface can tightly adhere to a matrix resin, with the result that the surface can sufficiently adhere to the interface with a resin. The ipa value is more preferably 0.07 to 0.20 $\mu A/cm^2$ and further preferably 0.10 to 0.18 $\mu A/cm^2$.

[0031] Furthermore, in the present invention, it is desirable that the amount of an oxygen containing functional group in a carbon fiber surface (obtained by X-ray photoelectron spectroscopy) be within the range of 0.05 to 0.15. This is because it is important to have an appropriate adhesiveness with a matrix resin at the interface.

[0032] Furthermore, in the present invention, a Si amount measured by ICP emission spectrometry is desirably 200 ppm or less. In order to manufacture a high-strength carbon fiber, usually an oil solution containing silicone oil is attached onto a precursor fiber bundle. Silicone oil has extremely excellent heat resistance properties and can impart excellent mold release characteristics. Thus, silicone oil is considered most suitable as an oil solution for a carbon-fiber precursor bundle, which is a multifilament bundle formed by assembling a large number of filaments each having an extremely small diameter and each being further subjected to a high-temperature treatment performed at a temperature of 200° C. or more for several tens of minutes to several hours. However, in carbonization treatment performed after stabilization treatment, the silicone oil is mostly decomposed and scattered. Consequently, the amount of silicone compound remaining on the

surface of a carbon fiber becomes extremely low. Furthermore, the remaining silicone compound, which is present near the surface of a carbon fiber, has been found to contribute to the formation of voids. Therefore, if the amount of such a silicone compound is reduced as much as possible, carbon fiber having few voids can be manufactured. As a result, the strength of a carbon fiber bundle can be increased. The more preferable Si amount is 150 ppm or less and a further preferable Si amount is 100 ppm or less.

(Precursor Fiber Bundle and Manufacturing Method Thereof)

[0033] The starting material for obtaining a carbon fiber bundle of the present invention is not particularly limited; however, the starting material that can be obtained from an acrylonitrile-based precursor fiber (hereinafter, appropriately referred to as "precursor fiber") is preferred from the viewpoint of developing mechanical performance.

[0034] The acrylonitrile-based copolymer constituting the precursor fiber is obtained from acrylonitrile (96 mass % or more) and several types of copolymerizable monomers. More preferably, the composition ratio of acrylonitrile is 97 mass % or more. Examples of copolymer components except acrylonitrile that are properly used include acrylic acid derivatives such as acrylic acid, methacrylic acid, itaconic acid, methyl acrylate and methyl methacrylate; and acryl amide derivatives such as acryl amide, methacryl amide, N-methyolacrylamide and N,N-dimethyl acrylamide and vinyl acetate. These may be used alone or in combination. A preferable copolymer is an acrylonitrile-based copolymer obtained by copolymerization of a monomer that has one or more carboxyl groups as an essential component.

[0035] As an appropriate method for copolymerizing a monomer mixture, any polymerization method may be used, including, for example, redox polymerization performed in an aqueous solution, suspension polymerization performed in non-homogeneous system and emulsion polymerization using a dispersant. Difference between the polymerization methods does not limit the present invention. The precursor fiber is preferably manufactured by dissolving the aforementioned acrylonitrile based polymer in an organic solvent such as dimethyl acetamide, dimethyl sulfoxide or dimethyl formamide to prepare dope. Since these organic solvents do not contain a metal component, the content of a metal component in the resultant carbon fiber bundle can be reduced. The solid substance concentration of the dope is preferably 20 mass % or more and more preferably 21 mass % or more.

[0036] The spinning method may be either wet spinning or dry-wet spinning. More preferably, dry-wet spinning is employed. In dry-wet spinning, the dope that is prepared is at first spun from a spinneret having numerous ejection holes arranged therein into the air and is then introduced into a congealed liquid filled with a solution mixture of an organic solvent and water whose temperature is controlled so that the dope will coagulate. The coagulated fiber is taken out, washed and drawn. As a washing method, any method may be used as long as the solvent can be removed. Note that, before the coagulated fiber that has been taken out is washed, if drawing is performed in the pre-drawing tank that contains a solvent whose concentration is lower than in congealed liquid and whose temperature is higher than that of congealed liquid, a fibril structure can be formed. When a coagulated fiber is drawn, the temperature of the drawing tank preferably falls within the range of 40 to 80° C. If the temperature is less than 40° C., a stable drawing cannot be secured and it causes the drawing to be poor, with the result that a uniform fibril structure cannot be formed. In contrast, if the temperature exceeds 80° C., excessively strong plasticizing action occurs by heat, and a solvent is rapidly removed from a fiber surface and the result is nonuniform drawing. Therefore, the quality of the precursor fiber bundle deteriorates. A more preferable temperature is 50 to 75° C. Furthermore, the concentration of the drawing tank is preferably 30 to 60 mass %. This is because if the concentration is less than 30 mass %, a stable drawing cannot be secured; whereas, if the concentration is beyond 60 mass %, an excessively large plasticization effect is obtained and interference with a stable drawing occurs. A more preferable concentration is 33 to 55 mass %.

[0037] The draw ratio in the drawing tank is preferably 2 to 4 times. If the draw ratio is less than twice, drawing is insufficient and a desired fibril structure cannot be formed. In contrast, if the draw ratio is beyond 4 times, a fibril structure itself is broken. The result is a precursor fiber bundle that has extremely low density. The draw ratio is more preferably 2.2 to 3.8 times and further preferably, 2.5 to 3.5 times.

[0038] Furthermore, after washing, if a fiber bundle that is processed in a swollen state without solvent is drawn in hot water, the orientation degree of the fiber can be further enhanced. If a relaxing step is slightly performed, distortion caused by drawing in the previous step can be removed. Preferably, in order to improve the orientation degree of a fiber by increasing the total draw ratio, drawing is performed in hot water at a ratio of 1.1 to 2.0 times.

[0039] Next, an oil solution composed of a silicone-based compound is attached so as to apply 0.8 to 1.6 mass % and the resultant fiber is subjected to dry densification. The dry densification is not particularly limited as long as dry densification is performed by a known drying method. Preferably, a method of passing a fiber through a plurality of heated rolls is employed.

[0040] The acrylic fiber bundle after the dry densification process has been performed, is, if necessary, drawn in pressurized steam of 130 to 200° C., in a dry heat medium of 100 to 200° C., between heated rolls of 150 to 220° C. or on a heat board up to 1.8 to 6.0 times. After the orientation degree is further improved and densification is performed, the fiber bundle is rolled up to obtain a precursor fiber bundle.

[0041] Furthermore, a carbon fiber bundle of the present invention can be manufactured from the above-mentioned precursor fiber bundle as follows. The precursor fiber bundle is fed to an oven for stabilization that is a type of furnace that circulates hot air at a temperature of 220 to 260° C. for 30 to 100 minutes to obtain a stabilized fiber having a density of 1.335 to 1.360 g/cm^3. At this time, an operation for extending the fiber by 0 to 10% is performed. The stabilization reaction consists of a cyclization reaction with heat and an oxidation reaction with oxygen. It is important to balance the two reactions. In order to balance the two reactions, time for performing stabilization treatment is preferably 30 to 100 minutes. If the reaction time is less than 30 minutes, a single fiber has a portion in which the oxidation reaction does not sufficiently proceed, within the fiber, with the result that a large structural variety is generated along the cross-section of the single fiber. As a result, the obtained carbon fiber has a structure that is non-uniformly formed and fails to develop high mechanical performance. In contrast, if the reaction time exceeds 100 minutes, a larger amount of oxygen will be present near the surface of a single fiber. Thereafter, in the following heat

treatment performed at a high temperature, a reaction that consumes an excessive amount of oxygen occurs to form a defective point. Because of this, high strength cannot be obtained. A more preferable stabilization treatment time is 40 to 80 minutes.

[0042] In the case where the density of a stabilized fiber is less than 1.335 g/cm^3, stabilization treatment is insufficient. In the following heat treatment performed at a high temperature, a decomposition reaction occurs to form a defective point. Because of this, high strength cannot be obtained. If the density of a stabilized fiber exceeds 1.360 g/cm^3, the oxygen content of the fiber increases. In the following heat treatment performed at a high temperature, a reaction that consumes an excessive amount of oxygen occurs to form a defective point. Because of this, high strength cannot be obtained. A more preferable density range of a stabilized fiber is 1.340 to 1.350 g/cm^3.

[0043] Appropriate extension of a fiber performed in an oven for stabilization is required in order to maintain and improve the orientation degree of a fibril structure that constitute a fiber. If the extension is less than 0%, the orientation degree of a fibril structure cannot be maintained; the orientation degree along the fiber axis is not sufficient for forming a carbon fiber structure; excellent mechanical performance cannot develop. In contrast, if the extension exceeds 10%, the fibril structure itself will be broken, with the result that formation of a carbon fiber structure will be impaired and the fracture point will change to a defective point. As a result, a carbon fiber that has high strength cannot be obtained. A more preferable extension rate is 3 to 8%.

[0044] Next, a stabilized fiber is passed through a first carbonization furnace of an inert atmosphere such as nitrogen that has a temperature gradient of 300 to 800° C., while extending it by 2 to 7%. A preferable processing temperature is 300 to 800° C. and the stabilized fiber is processed under linear temperature gradient conditions. Taking into consideration the temperature in the stabilization treatment step, the initiation temperature is preferably 300° C. or more. If the highest temperature exceeds 800° C., the fiber that is processed becomes very fragile and it is difficult to operate the following step. A more preferable temperature range is 300 to 750° C. The temperature gradient is not particularly limited; however a linear gradient is preferably employed.

[0045] If the extension rate is less than 2%, orientation of a fibril structure cannot be maintained and the orientation degree along the fiber axis in formation of a carbon fiber structure will not be sufficient, with the result that excellent mechanical performance cannot develop. In contrast, if the extension rate exceeds 7%, a fibril structure itself is broken, with the result that formation of a carbon fiber structure will be impaired and a fracture point will change to a defective point. As a result, a carbon fiber having high strength cannot be obtained. A more preferable extension rate is 3 to 5%.

[0046] In the first carbonization furnace, a preferable heat treatment time is 1.0 to 3.0 minutes. If the treatment time is less than 1.0 minute, the temperature will abruptly increase, and this will be accompanied by a severe decomposition reaction. As a result, a carbon fiber that has high strength cannot be obtained. If the treatment time exceeds 3.0 minutes, effect of plasticization in the former step will be produced, with the result that the orientation degree of a crystal will tend to decrease. As a result the mechanical performance of the resultant carbon fiber will be impaired. A more preferable heat treatment time is 1.2 to 2.5 minutes.

[0047] Furthermore, the stabilized fiber is subjected to a second carbonization furnace that has an inert atmosphere such as nitrogen having a temperature gradient of 1000 to 1600° C. and is treated under heat under tension to obtain a carbon fiber. Furthermore, if necessary, the carbon fiber is optionally subjected to a third carbonization furnace having a desired temperature gradient and is treated with heat in an inert atmosphere under tension.

[0048] The temperature for carbonization treatment is determined depending upon the desired elastic modulus of a carbon fiber. In order to obtain a carbon fiber that has high strength property, the highest temperature of carbonization treatment is preferably low. Furthermore, elastic modulus can be increased by increasing the treatment time. As a result, the highest temperature can be reduced. Moreover, the gradient of temperature can be set to change gradually by increasing the treatment time. This is effective in suppressing defective point formation. The temperature of the second carbonization furnace varies depending upon the temperature of the first carbonization furnace; however, the temperature is acceptable as long as it is a temperature of 1000° C. or more and preferably 1050° C. or more. The temperature gradient is not particularly limited; however it is preferably set to change linearly.

[0049] In the second carbonization furnace, the heat treatment time is preferably 1.3 to 5.0 minutes and more preferably 2.0 to 4.2 minutes. In the heat treatment, the fiber significantly shrinks during processing. Thus, it is important to perform heat treatment under tension.

[0050] An extension rate is preferably −6.0 to 0.0%. If the extension rate is less than −6.0%, the orientation of a crystal in the fiber-axis direction is not satisfactory and sufficient performance cannot be obtained. In contrast, if the extension rate exceeds 0.0%, the structure so far formed itself is broken and defective points are significantly formed, with the result that the strength is significantly reduced. More preferably, the extension rate ranges −5.0% to −1.0%.

[0051] Next, the carbon fiber bundle is subjected to surface oxidization treatment. Examples of the surface treatment method include known methods, i.e., oxidation treatments such as electrolytic oxidation, chemical oxidation and air oxidation. Any one of these methods may be employed. The electrolytic oxidation treatment industrially widely used is preferred since surface oxidization treatment can be stably performed. In addition, to control the ipa value, which represents a preferable surface treatment state in the present invention, so that the ipa value falls within the aforementioned range, performing the electrolytic oxidation treatment while varying electric quantity is the simplest method. In this case, even if the electric quantity is the same, the ipa value significantly varies depending upon the electrolyte and the concentration thereof that is used. In the present invention, electrolytic oxidation treatment can be performed preferably in an aqueous alkaline solution of pH>7 with a carbon fiber as an anode while supplying an electric quantity of 10 to 200 coulomb/g. By using oxidation treatment, the ipa value of 0.05 to 0.25 μA/cm^2 can be obtained. Examples of electrolyte that is preferably used include ammonium carbonate, ammonium bicarbonate, calcium hydroxide, sodium hydroxide and potassium hydroxide.

[0052] Next, the carbon fiber bundle of the present invention is subjected to sizing treatment. The sizing agent is dissolved in an organic solvent or dispersed in water with the help of an emulsifier to prepare an emulsion solution. The

above preparation is applied to a carbon fiber bundle in accordance with a roller dip method, a roller contact method, etc. Subsequently, the carbon fiber bundle is dried. In this manner, sizing treatment can be performed. Note that the amount of the sizing agent attached to the surface of a carbon fiber can be controlled by controlling the concentration of the sizing agent solution and the squeeze amount thereof. Furthermore, drying can be performed by use of hot air, a hot plate, a heating roller and various infrared heaters.

[0053] The most preferable sizing agent composition to be applied to the surface of the carbon fiber of the present invention is a urethane modified epoxy resin, which is a reaction product of (a) an epoxy resin that contains a hydroxy group (hereinafter appropriately referred to as a component (a)), (b) a polyhydroxy compound (hereinafter appropriately referred to as a component (b)) and (c) a diisocyanate that contains an aromatic ring (hereinafter appropriately referred to as a component (c)). Furthermore, a mixture of a urethane modified epoxy resin, which is a reaction product that is obtained by introducing a larger amount of component (a) than is required for a reaction system, and component (a) that remains is mentioned.

[0054] Moreover, a mixture of a urethane modified epoxy resin obtained by using an epoxy resin having no hydroxy group (hereinafter appropriately referred to as component (d)) and component (d) is mentioned. Also, a mixture of a urethane modified epoxy resin, component (a) and component (d) is mentioned.

[0055] An epoxy group has a very strong interaction with an oxygen-containing functional group present in a carbon fiber surface and thus can strongly allow a sizing-agent component to adhere to the carbon fiber surface. Furthermore, since a urethane bonding unit, which is produced from a polyhydroxy compound and a diisocyanate that contains an aromatic ring, is contained, flexibility and strong interaction with a carbon fiber surface due to the polarity of a urethane bond and an aromatic ring can be imparted. Accordingly, the urethane modified epoxy resin that has an epoxy group and the above urethane bonding unit is a compound that is capable of strongly bonding to a carbon fiber surface and that has flexibility. In other words, such a sizing agent composition forms a flexible interface layer that strongly adheres to a carbon fiber surface. Thus, the mechanical performance of the composite material obtained by impregnating a carbon fiber with a matrix resin and cuing the resin can be improved.

[0056] The component (a) is not particularly limited, and the number of hydroxy groups contained in the component (a) is not limited. For example, glycidol, methyl glycidol, bisphenol type F epoxy resin, bisphenol type A epoxy resin and oxycarboxylic acid glycidyl ester epoxy resin can be used. A particular preferable resin is a bisphenol type epoxy resin. Since these resins have an aromatic ring, they interact strongly with a carbon fiber surface. Furthermore, in view of heat resistance and rigidity, an epoxy resin having an aromatic ring is often used as the matrix resin in a composite material. This is because compatibility with such a matrix resin is excellent.

[0057] As component (a), two types or more epoxy resins can be used.

[0058] Furthermore, component (b) is preferably constituted of any one from among an adduct of bisphenol A with an alkylene oxide, an aliphatic polyhydroxy compound and a polyhydroxymonocarboxy compound or a mixture of these. This is because these compounds can soften the aforementioned urethane modified epoxy resins. Specific examples thereof include an adduct of bisphenol A with 4 to 14 mol of ethylene oxide, an adduct of bisphenol A with 2 to 14 mol of propylene oxide, an adduct of bisphenol A with ethylene oxide-propylene oxide block copolymer, polyethylene glycol, trimethylolpropane and dimethylolpropionic acid.

[0059] Furthermore, component (c) is not particularly limited and a particular preferable component is toluene diisocyanate or xylene diisocyanate.

[0060] Furthermore, an epoxy resin that serves as component (d) is not particularly limited. Preferably, an epoxy resin having two or more epoxy groups in a molecule is employed. This is because the surface of a carbon fiber strongly interacts with an epoxy group and thus these compounds strongly adhere to the surface. The type of epoxy group is not particularly limited and a glycidyl type, an alicyclic epoxy group, etc. can be employed. Examples of preferable epoxy resin that can be used include a bisphenol type-F epoxy resin, a bisphenol type-A epoxy resin, a novolak-type epoxy resin, a dicyclopentadiene type epoxy resin (Epiclon HP-7200 series: manufactured by DIC Corporation), tris(hydroxyphenyl) methane-type epoxy resin (Epicoat 1032H60, 1032S50: manufactured by Japan Epoxy Resins Co., Ltd.), DPP Novolak type epoxy resin (Epicoat 157S65, 157S70: manufactured by Japan Epoxy Resins Co., Ltd.) and bisphenol A alkylene oxide-added epoxy resin.

[0061] In manufacturing the mixture that contains component (d), when component (a), component (b) and component (c) are reacted, component (d) may be added simultaneously with component (a). Alternatively, after completion of the urethanization reaction, component (d) may be added. As a water dispersion that contains these compounds, HYDRAN N320 (manufactured by DIC) is mentioned.

[0062] The carbon fiber bundle of the present invention that has a strand elastic modulus of 250 GPa or more is obtained through a carbonizing process performed at relatively high temperature. Accordingly, it is beneficial that the carbon fiber is obtained from a precursor fiber that contains as few impurities such as a metal as possible. The amount of metal content in the resultant carbon fiber bundle is preferable small. In particular, the total amount of metal components including alkaline metal, alkaline earth metal, zinc, iron and aluminum is preferably 50 ppm or less. These metals react with carbon, melt or vaporize at a temperature beyond 1000° C., and this constitutes a reason why defective points are formed. Highly strong carbon fiber cannot be manufactured.

EXAMPLES

[0063] Now, the present invention will be described in detail by way of Examples. Note that, performance of a carbon fiber bundle in Examples was measured and evaluated in accordance with the following method.

[0064] <1. Measurement of Uneven Surface Structure of Single Fiber>

[0065] The uneven surface structure can be measured based on the shape of the surface as follows:

[0066] Several single-fibers of a carbon fiber bundle were placed on a sample stand and immobilized at both ends. Furthermore, Dotite was applied around the fibers to prepare a measurement sample. A range of 1000 nm in the circumference direction of a single fiber was scanned by an atomic force microscope (SPI3700/SPA-300 (trade name) manufactured by Seiko Instruments Inc.) using a cantilever formed of silicon nitride, in an AFM mode while sliding little by little at

a distance of 1000 nm in the fiber-axis direction. From the resultant measured image, a low-frequency component was cut off in accordance with a two-dimensional Fourier transform and thereafter subjected to inverse transformation. From the resultant planar image of a cross-section from which curvature of the single fiber was removed, an area range surrounded by a length of 1.0 μm in the fiber-circumference direction and a length of 1.0 μm in the fiber-axis direction was selected and the difference in height between the highest portion and the lowest portion was read out, and Ra is obtained by making a calculation in accordance with the following expression (2).

$$Ra=\{1/(Lx\times Ly)\}\cdot\int^{Ly}_{0}\int^{LX}_{0}|f(x,y)|dxdy \quad (2)$$

[0067] "Center surface": A plane which is parallel to the plane that has a minimum deviation of the height from the place to the actual surface and that divides the actual surface equally into two based on volume. In other words, the portion that is surrounded by the plane and the actual surface, volumes V1 and V2 that correspond to both side portions of the plane are equal to each other.

[0068] "f(x, y)": Difference in height between the actual surface and the center surface,

[0069] "Lx, Ly": Size of the XY plane.

[0070] Furthermore, when an atomic force microscope was used to take measurements, the presence or absence of an uneven structure of 0.6 μm or more in length was checked and the length of an uneven structure of 300 nm or less in length was measured.

[0071] <2. Evaluation of a Cross-Sectional Shape of Single Fiber>

[0072] The ratio of the major axis and the minor axis (major axis/minor axis) of the cross section of single fibers that constitute a carbon fiber bundle was determined as follows:

[0073] A carbon fiber bundle for measurement was passed through a tube formed of a vinyl chloride resin that has an inner diameter of 1 mm. The tube was cut in the shape of a circle by a knife to prepare samples. Subsequently, each sample was allowed to adhere to a SEM sample stand so that the cross-section faced up; Au was deposited in a thickness of about 10 nm by sputtering; and a fiber cross-section was observed by a scanning electron microscope (product name: XL20, manufactured by Philips) under the following conditions: an acceleration voltage of 7.00 kV and a migration distance of 31 mm to measure the major axis and minor axis of the cross section of the single fiber.

[0074] <3. Evaluation of Strand Physical Properties of Carbon Fiber Bundle>

[0075] Preparation of a strand test sample of a carbon fiber bundle impregnated with a resin and measurement of the strength of the sample were performed in accordance with JIS R7601. However, the elastic modulus was calculated in the range of strain in accordance with ASTM.

[0076] <4. Measurement of Knot Tenacity of Carbon Fiber Bundle>

[0077] Knot tenacity was measured as follows:

[0078] To both ends of a carbon fiber bundle of 150 mm in length, a grip portion of 25 mm in length was attached to prepare a test sample. In preparing the test sample, a load of 0.1×10^{-3} N/denier was applied to unidirectionally arrange carbon fiber bundles. In the test sample, a single knot was formed almost in the center. Tension was performed at a crosshead rate of 100 mm/min. Twelve bundles were used for a test. The smallest value and the largest value were removed and the average value of 10 bundles was obtained and used as a measurement value.

[0079] <5. Evaluation of "Surface Energy of Surface Formed by Fracture" of Carbon Fiber Bundle>

[0080] A single carbon fiber was cut into pieces in the length of 20 cm. Each of the single-fiber pieces was allowed to adhere and immobilize onto a mount for a tensile test for a single fiber of 10-mm sample length shown in JIS R7606. An extra portion extruded from the mount was cut and removed. In this manner, samples were prepared.

[0081] Next, these samples that were fixed to the mount were irradiated with a laser to obtain a hemispherical defect. As a laser interface system, MicroPoint (pulse energy 300 μJ) manufactured by Photonic Instruments Co., Ltd. were used. As the optical microscope required for converging laser light, ECLIPSE LV100 manufactured by Nikon was used. The aperture stop of the optical microscope was set to a minimum and an object lens was set at 100 times. Under the conditions, a laser (one pulse) having a wavelength of 435 nm, the intensity of which was attenuated by 10% by an attenuator, was applied to the center of a sample in the fiber-axis direction and in the perpendicular direction of the fiber axis to form a hemispherical defect.

[0082] To avoid shrinkage break of a sample carbon fiber, the sample that was attached to a mount was further sandwiched by films and the space within the films was filled with viscous liquid and then subjected to a tensile test. To describe more specifically, a film of about 5 mm in width and about 15 mm in length was prepared and allowed to adhere to the upper portion of both surfaces of the sample mount with an adhesive and sandwiched so as to wrap the sample including the mount. The space within the film was filled with an aqueous glycerin solution (glycerin:water=1:2). A tensile test was performed at a tension rate of 0.5 mm/min to measure the breaking load.

[0083] Next, a sample of a pair of pieces, which was divided into two pieces in the tensile test, was removed from the mount, carefully washed with water and naturally dried. Subsequently, a sample piece was immobilized onto a SEM sample stand with carbon paste so that the fracture was in a face up position to enable the preparation of a sample for SEM observation. The fracture surface of the obtained sample for SEM observation was observed by SEM, i.e., JSM6060 (acceleration voltage: 10 to 15 kV, magnification: 10000 to 15000) manufactured by JEOL Ltd.

[0084] The obtained SEM image was imported into a personal computer and analyzed by image analyzing software. In this manner, the size of a hemispherical defect and the cross-sectional area of a fiber were measured.

[0085] Next, breaking strength (a) (breaking load/fiber cross-sectional area) and the size of a hemispherical defect (C) were plotted. The slope of the data was obtained.

$$\sigma=(2E/\pi C)^{1/2}\times(\text{surface energy of surface formed by fracture})^{1/2} \quad (1)$$

[0086] In accordance with Equation (1), surface energy of surface formed by fracture was obtained from the slope and ultrasonic elastic modulus (E) of a carbon fiber bundle.

[0087] <6. Measurement of Ipa of Carbon Fiber Bundle>

[0088] An Ipa value was measured by the following method.

[0089] An electrolyte is adjusted to pH3 with a 5% aqueous phosphoric acid solution and bubbled with nitrogen to eliminate the effect of dissolved oxygen. A sample carbon fiber

was dipped in the electrolyte as one of the electrodes, whereas, a platinum electrode having a sufficient surface area is used as the other electrode. Herein, as a reference electrode, an Ag/AgCl electrode was employed. A sample was formed of a 12000-filament tow having a length of 50 mm. The potential to be applied between the carbon fiber electrode and the platinum electrode ranges from −0.2 V from +0.8 V and a scanning speed thereof was set to be 2.0 mV/sec. A current-voltage curve was drawn by an X-Y recorder. After sweeping was performed three times or more to obtain a stable curve, a current value i was read with a potential of +0.4 V applied to the Ag/AgCl reference electrode that was used as a reference potential, and an ipa value was calculated in accordance with the following expression (3).

$$ipa = 1(\mu A)/\text{sample length(cm)} \times \{4\pi \times \text{weight per unit area(g/cm)} \times \text{number of filaments/density(g/cm}^3)\}^{1/2} \quad (3)$$

[0090] The apparent surface area was calculated from sample length, sample density obtained by the method described in JIS R7601 and mass per unit area. Current value i was divided by the obtained value to obtain an ipa value. The measurement was performed by cyclic voltammetry analyzer Type P-1100 manufactured by Yanagimoto Mfg. Co., Ltd.

[0091] <7. Measurement of Si Amount of Carbon Fiber Bundle>

[0092] A sample of a carbon fiber bundle was placed in a platinum crucible whose tare was known and calcified in a muffle furnace of 600 to 700° C. The mass thereof was measured to obtain ash content. Subsequently, a predetermined amount of sodium carbonate was added, and the mixture was melted by a burner and dissolved with deionized water in a 50 ml poly measuring flask. The sample was measured by ICP emission spectrometry to determine the amount of Si.

Production Examples 1 to 7 of Precursor Fiber Bundle

Precursor Fiber (1)

[0093] An acrylonitrile based polymer containing acrylonitrile (98 mass %) and methacrylic acid (2 mass %) was dissolved in dimethylformamide to prepare a 23.5 mass % dope.

[0094] The dope was ejected from a spinneret having 0.15 mm diameter with 2000 ejection holes arranged therein in a dry-wet spinning manner. To explain more specifically, the dope was ejected into the air, passed through a space of about 5 mm and then solidified in a congealed liquid filled with an aqueous solution containing 79.0 mass % dimethyl formamide and controlled at a temperature of 10° C. to obtain a coagulated fiber. Subsequently, the coagulated fiber was drawn (1.1 times) in the air and drawn (2.5 times) in a drawing tank filled with an aqueous solution containing 35 mass % dimethyl formamide and controlled at 60° C. After the drawing process, the fiber bundle in which a solvent was present was washed with clean water and then drawn (1.4 times) in hot water of 95° C. Sequentially, to the fiber bundle, an oil solution containing an amino modified silicone as a main component was attached so as to apply 1.1 mass %, dried and densified. After the drying and densification step, the fiber bundle was drawn (2.6 times) between heated rolls to further improve the orientation degree and densification. Thereafter, the bundle was wound up to obtain an acrylonitrile-based precursor fiber bundle. The denier of the fiber was 0.77 dtex.

Precursor Fiber (2)

[0095] Precursor fiber bundle (2) was obtained under the same conditions as in precursor fiber bundle (1) except that the draw ratio before washing with water was set to be 2.9 times and the draw ratio in hot water after washing was set to be 1.2 times.

Precursor Fiber (3)

[0096] Precursor fiber bundle (3) was obtained under the same conditions as in precursor fiber bundle (2) except that the denier of the precursor fiber was set to be 0.67 dtex.

Precursor Fiber (4)

[0097] Precursor fiber bundle (4) was obtained under the same conditions as in precursor fiber bundle (2) except that the denier of the precursor fiber was set to be 0.90 dtex.

Precursor Fiber (5)

[0098] Precursor fiber bundle (5) was obtained under the same conditions as in precursor fiber bundle (1) except that the draw ratio before washing with water was set to be 4.1 times, the draw ratio in hot water after washing was set to be 0.9 times and drawing that was performed between heated rolls was set to be 2.4 times.

Precursor Fiber (6)

[0099] Precursor fiber bundle (6) was obtained under the same conditions as in precursor fiber bundle (1) except that the draw ratio before washing with water was set to be 1.9 times and the draw ratio in hot water after washing was set to be 2.0 times.

Precursor Fiber (7)

[0100] Precursor fiber bundle (7) was obtained under the same conditions as in precursor fiber bundle (2) except that the denier of the precursor fiber was set to be 1.0 dtex.

[0101] The manufacturing conditions for precursor fiber bundles (1) to (7) are shown in Table 1.

TABLE 1

	Spinning conditions								Precursor
	Coagulation bath		In the air	Draw tank			Hot water	Dry heat	fiber
Precursor fiber	Temperature (° C.)	Concentration (%)	Draw ratio	Temperature (° C.)	Concentration (%)	Draw ratio	Draw ratio	drawing Ratio	Denier dtex
Precursor (1)	10	79.0	1.1	60	35	2.5	1.4	2.6	0.77
Precursor (2)	10	79.0	1.1	60	35	2.9	1.2	2.6	0.77

TABLE 1-continued

	Spinning conditions								Precursor
	Coagulation bath		In the air	Draw tank			Hot water	Dry heat	fiber
Precursor fiber	Temperature (° C.)	Concentration (%)	Draw ratio	Temperature (° C.)	Concentration (%)	Draw ratio	Draw ratio	drawing Ratio	Denier dtex
Precursor (3)	10	79.0	1.1	60	35	2.9	1.2	2.6	0.67
Precursor (4)	10	79.0	1.1	60	35	2.9	1.2	2.6	0.90
Precursor (5)	10	79.0	1.1	60	35	4.1	0.99	2.4	0.77
Precursor (6)	10	79.0	1.1	60	35	1.9	2.0	2.4	0.77
Precursor (7)	10	79.0	1.1	60	35	2.9	1.2	2.6	1.00
Precursor (8)	5	77.0	1.3	60	0	2.0	2.0	1.9	0.77

Examples 1 to 7, Comparative Examples 1 to 4

Preparation of Carbon Fiber Bundle

[0102] A plurality of precursor fiber bundles (1), (2), (3), (4), (5), (6) or (7) were arranged in parallel and introduced in an oven for stabilization. Air heated to 220 to 280° C. was sprayed to the precursor fiber bundles to perform stabilization treatment. In this manner, stabilized fiber bundles having a density of 1.345 g/cm^3 were obtained. The extension rate was set to be 6% and stabilization treatment time was 70 minutes.

[0103] Next, the stabilized fiber bundles were passed through a first carbonization furnace having a temperature gradient of 300 to 700° C. in nitrogen while the extension rate was increased by 4.5%. The temperature gradient was set so as to change linearly. The treatment time was 2.0 minutes.

[0104] Furthermore, heat treatment was performed using a second carbonization furnace having a nitrogen atmosphere in which the temperature gradient of 1000 to 1600° C. could be set, at the predetermined temperatures shown in Table 2 or Table 3. Subsequently, heat treatment was performed using a third carbonization furnace having a nitrogen atmosphere in which the temperature gradient of 1200 to 2400° C. could be set, at the predetermined temperatures shown in Table 2 or Table 3 to obtain carbon fiber bundles. The total extension rate of the fiber bundles through the treatments in the second carbonization furnace and third carbonization furnace was −4.0%, and the treatment time in total was set to be 3.5 minutes.

[0105] Subsequently, the fiber bundles were fed to a 10 mass % aqueous ammonium bicarbonate solution. Current was supplied between a carbon fiber bundle serving as an anode and a counter pole so as to obtain a quantity of electricity of 40 coulombs per carbon fiber (1 g) to be treated. Then, the fiber bundles were washed with warm water of 90° C. and dried.

[0106] Next, Hydran N320 (hereinafter referred to as "sizing agent 1") was attached onto the fiber bundles in the amount of 0.5 mass % and wound by a bobbin to obtain a carbon fiber bundle.

(Preparation of UniDirectional Prepreg)

[0107] Onto a mold-releasing paper coated with epoxy resin #410 (that can be used at 180° C.) [manufactured by Mitsubishi Rayon Co., Ltd.] in the B stage, 156 carbon fiber bundles released from a bobbin were arranged in parallel and passed through a heat compression roller. In this manner, the carbon fiber bundles were impregnated with epoxy resin. A protecting film was laminated on the resultant bundles to prepare a prepreg arranged in a unidirection (hereinafter referred to as a "UD prepreg") having a resin content of about 33 mass %, a carbon fiber mass per unit area of 125 g/m^2 and a width of 500 mm.

(Molding of a Laminate Board and Evaluation of Mechanical Performance)

[0108] A laminate board was prepared by using the UD prepreg and the tensile strength of the laminate board at angle 0° was evaluated by the evaluation method in accordance with ASTM D3039.

[0109] The manufacturing conditions for a carbon fiber bundle and the evaluation results are shown in Table 2 and Table 3.

[0110] Note that it was confirmed that in any of Examples, a single fiber does not have an uneven surface structure that has a length of 0.6 μm or more and that extends in the longitudinal direction of a fiber but has a microscopic uneven structure that has a length of 300 nm or less.

TABLE 2

Carbon fiber bundle	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Type of precursor fiber bundle	Precursor (1)	Precursor (2)	Precursor (3)	Precursor (4)	Precursor (2)	Precursor (2)	Precursor (2)	Precursor (2)
Conditions of second carbonization furnace (° C.)	1250-1300	1250-1300	1250-1300	1250-1300	1050-1250	1100-1301	1200-1500	1050-1250

TABLE 2-continued

Carbon fiber bundle	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Conditions of third carbonization furnace (° C.)	1350-1550	1350-1550	1350-1550	1350-1550	1250-1450	1300-1501	1550-1800	—
Difference in height (Rp − v) (nm)	12	15	14	16	15	15	15	15
Ra (nm)	3	4	3	4	4	4	4	4
Major axis/minor axis of cross-section	1.005	1.005	1.005	1.005	1.005	1.005	1.005	1.005
Weight per unit area of single fiber (mg/m)	0.035	0.035	0.030	0.041	0.035	0.035	0.035	0.035
Strand strength (MPa)	6050	6300	6400	6100	6700	6500	6050	6350
Strand elastic modulus (GPa)	330	335	345	325	305	325	355	260
Knot tenacity (N/mm^2)	950	1040	1100	1000	1200	1100	910	1250
Surface energy of surface formed by fracture (N/m)	32	33	34	33	35	34	30	36
iPa ($\mu A/cm^2$)	0.15	0.15	0.15	0.15	0.17	0.16	0.09	0.18
O1S/C1S	0.09	0.09	0.09	0.09	0.11	0.1	0.07	0.13
Si amount (ppm)	150	120	110	130	120	120	125	120
Metal content (ppm)	40	40	40	40	40	40	40	40
Tensile strength of laminate board at 0° C. (in terms of 60 vol %) MPa	3000	3150	3180	3100	3400	3300	3020	3240

TABLE 3

Carbon fiber bundle	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Type of precursor fiber bundle	Precursor (5)	Precursor (6)	Precursor (7)	Precursor (6)	Precursor (8)
Conditions of second carbonization furnace (° C.)	1250-1300	1250-1300	1250-1300	1200-1500	1250-1300
Conditions of third carbonization furnace (° C.)	1350-1550	1350-1550	1350-1550	1550-1800	1350-1550
Difference in height(Rp − v) (nm)	29	13	23	13	8
Ra (nm)	8	3	6	3	2
Major axis/minor axis of cross-section	1.005	1.005	1.005	1.005	1.005
Weight per unit area of single fiber (mg/m)	0.035	0.035	0.045	0.045	0.045
Strand strength (MPa)	5400	5700	5750	5200	5950
Strand elastic modulus (GPa)	330	330	315	355	325
Knot tenacity (N/mm^2)	650	750	850	630	790
Surface energy of surface formed by fracture (N/m)	29	30	30	28	29
iPa ($\mu A/cm^2$)	0.18	0.15	0.15	0.09	0.15
O1S/C1S	0.12	0.10	0.09	0.07	0.11
Si amount (ppm)	300	220	160	210	230
Metal content (ppm)	40	40	40	40	40
Tensile strength of laminate board at 0° C. (in terms of 60 vol %) MPa	2650	2700	2700	2400	2850

Production Example 8 of Precursor Fiber Bundle

[0111] A dope, which was prepared in the same manner as in Production Example 1, was ejected from a spinneret having 0.13 mm diameter with 2000 of ejection holes arranged therein in a dry-wet spinning manner. To explain more specifically, the dope was ejected into the air, passed through a space of about 5 mm and then solidified in a congealed liquid filled with an aqueous solution containing 77.0 mass % dimethyl formamide and controlled at a temperature of 5° C. to obtain a coagulated fiber. Subsequently, the coagulated fiber was drawn (1.3 times) in the air and drawn (2.0 times) in a drawing tank filled with an aqueous solution controlled at 60° C. After the drawing process, the fiber bundle in which a solvent was present was washed with clean water and then drawn (2.0 times) in hot water of 95° C. Sequentially, to the fiber bundle, an oil solution containing an amino modified silicone as a main component was attached so as to apply 1.0 mass %, dried and densified. After the drying and densification step, the fiber bundle was drawn (1.9 times) between heated rolls to further improve the orientation degree and densification. Thereafter, the bundle was wound up to obtain the precursor fiber bundle. The denier of the fiber was 0.77 dtex.

Example 8

[0112] A carbon fiber bundle was prepared under the same carbonizing conditions as in Example 5 except that the third carbonization furnace was not used. Furthermore, a laminate board was prepared in the same manner and mechanical performance was evaluated to obtain the results shown in Table 2. Note that, it was confirmed that the single fiber has no uneven surface structure having a length of 0.6 μm or more and extending in the longitudinal direction of the fiber and has an uneven microscopic structure having a length of 300 nm or less.

Examples 9 to 11, Comparative Examples 6 to 8

[0113] Carbon fiber bundles were obtained in the same manner as in Example 2 except that the carbonizing conditions were changed. The evaluation results are shown in Table 4. Note that, in any one of Examples, it was confirmed that the single fiber has no uneven surface structure having a length of 0.6 μm or more and extending in the longitudinal direction of the fiber and has an uneven microscopic structure having a length of 300 nm or less.

TABLE 4

Carbon fiber bundle	Example 9	Comparative Example 6	Example 10	Comparative Example 7	Example 11	Comparative Example 8
Conditions changed from Example 2	Stabilized fiber extension rate	Stabilized fiber extension rate	First carbonated fiber extension rate	First carbonated fiber extension rate	Second, third carbonated fiber extension rate	Second, third carbonated fiber extension rate
	8.0%	10.5%	6.5%	7.2%	−5.2%	−6.5%
Difference in height(Rp − v) (nm)	13	12	14	13	15	16
Ra (nm)	4	4	4	4	4	4
Major axis/minor axis of cross-section	1.005	1.005	1.005	1.005	1.005	1.005
Weight per unit area of single fiber (mg/m)	0.034	0.033	0.034	0.033	0.035	0.035
Strand strength (MPa)	6000	5300	5900	5400	6050	5500
Strand elastic modulus (GPa)	338	340	336	336	327	310
Surface energy of surface formed by fracture (N/m)	990	700	970	750	990	800
Knot tenacity (N/mm^2)	31	27	30	28	31	30
iPa ($\mu A/cm^2$)	0.15	0.15	0.15	0.15	0.15	0.15
O1S/C1S	0.09	0.09	0.09	0.09	0.09	0.09
Si amount (ppm)	120	120	120	120	120	120
Metal content (ppm)	40	40	40	40	40	40
Tensile strength of laminate board at 0° C. (in terms of 60 vol %) MPa	3000	2550	2950	2500	2980	2600

Examples 12 and 13

[0114] Carbon fiber bundles were obtained in the same manner as in Example 5 except that the surface treatment conditions were changed. The evaluation results are shown in Table 5. Note that in any of the Examples, it was confirmed that the single fiber has no uneven surface structure having a length of 0.6 μm or more and extending in the longitudinal direction of the fiber and has an uneven microscopic structure having a length of 300 nm or less.

Examples 14 to 16

[0115] Carbon fiber bundles were obtained in the same manner as in Example 5 except that the types and amounts attached of sizing agents were changed. The evaluation results are shown in Table 5. Note that in any one of the Examples, it was confirmed that the single fiber has no uneven surface structure having a length of 0.6 μm or more and extending in the longitudinal direction of the fiber and has an uneven microscopic structure having a length of 300 nm or less.

[0116] Note that, sizing agent 2, sizing agent 3 and sizing agent 4 were prepared as follows:

(Sizing Agent 2)

[0117] "Epicoat 828" (80 parts by mass) manufactured by Japan Epoxy Resins Co., Ltd. as a main agent and "Pluronic F88" (20 parts by mass) manufactured by ADEKA Corporation as an emulsifier were blended to obtain an aqueous dispersion by phase-transfer emulsification.

(Sizing Agent 3)

[0118] In a flask, polyol (3.2 mol) consisting of 1.8 mol of an adduct of bisphenol A with 8 mol of propylene oxide, 0.8 mol of trimethylolpropane and 0.6 mol of dimethyloipropionic acid were placed. Furthermore, 0.5 g of 2,6-di(t-butyl) 4-methylphenol (BHT) as a reaction inhibitor and 0.2 g of dibutyltin dilaurate as a reaction catalyst were added and stirred until a homogeneous mixture was obtained. Herein, if necessary, methyl ethyl ketone was added as a viscosity moderator. To the mixture homogeneously dissolved, metaxylene diisocyanate (3.4 mol) was added dropwise and polymerization of a urethane prepolymer was performed while stirring at a reaction temperature of 50° C. for a reaction time of 2 hours. Then, Epicoat 834 (manufactured by JER) (0.25 mol) was added and reacted with an isocyanate group at an end of the urethane prepolymer to obtain an epoxy modified urethane resin.

[0119] The epoxy modified urethane resin (90 parts by mass) and "Pluronic F88" (10 parts by mass) manufactured by ADEKA Corporation as an emulsifier were blended to prepare an aqueous dispersion.

(Sizing Agent 4)

[0120] To a flask, polyethylene glycol 400 (2.5 mol) and Epicoat 834 (manufactured by JER) (0.7 mol) were placed and further 2,6-di(t-butyl)-4-methylphenol (BHT) (0.25 g) as a reaction inhibitor, and dibutyl tin dilaurate (0.1 g) as a reaction catalyst were added. The mixture was stirred until it became homogeneous. Herein, if necessary, methyl ethyl ketone was added as a viscosity moderator. To the mixture homogeneously dissolved, a metaxylene diisocyanate (2.7 mol) was added dropwise. The reaction was performed at a temperature of 40° C. for 2 hours while stirring to obtain an epoxy modified urethane resin.

[0121] The epoxy modified urethane resin (80 parts by mass) and Pluronic F88 (20 parts by mass) manufactured by ADEKA Corporation as an emulsifier were mixed to prepare an aqueous dispersion.

TABLE 5

Carbon fiber bundle	Example 12	Example 13	Example 14	Example 15	Example 16
Conditions changed from Example 5	Surface treatment 8% Ammonium carbonate 20 coulomb/g	Surface treatment Ammonium bicarbonate 200 coulomb/g	Sizing agent Sizing agent 2 (amount attached, 0.4 mass %)	Sizing agent Sizing agent 3 (amount attached, 0.4 mass %)	Sizing agent Sizing agent 4 (amount attached, 0.4 mass %)
Strand strength (MPa)	6,400	6,700	6,700	6,700	6,700
iPa ($\mu A/cm^2$)	0.40	0.24	0.17	0.17	0.17
O1S/C1S	0.19	0.16	0.11	0.11	0.11
Tensile strength of laminate board at 0° C. (in terms of 60 vol %) MPa	3000	3280	3050	3410	3350

INDUSTRIAL APPLICABILITY

[0122] The carbon fiber bundle of the present invention can be used as a constructional material for airplanes and high speed moving bodies.

1. A carbon fiber bundle formed of the single carbon fiber: each single carbon fiber having has no uneven surface structure that has a length of 0.6 μm or more and that extends in the longitudinal direction of the single fiber, each single carbon fiber having an uneven structure in which the difference in height (Rp−v) between a highest portion and a lowest portion of the surface of the single fiber is 5 to 25 nm, and in which an average roughness Ra is 2 to 6 nm, and each of which has a ratio of 1.00 to 1.01 of a major axis to a minor axis (major axis/minor axis) of a cross-section of the single fiber; wherein a mass of the single fiber per unit length falls within the range of 0.030 to 0.042 mg/m; a strand strength is 5900 MPa or more; a strand elastic modulus measured by the ASTM method is 250 to 380 GPa; and a knot tenacity is 900 N/mm^2 or more.

2. A carbon fiber bundle formed of the single carbon fiber: each single carbon fiber having no uneven surface structure that has a length of 0.6 μm or more and that extends in the longitudinal direction of the single fiber, each single carbon fiber having an uneven structure that has a length of 300 nm or less in which the difference in height (Rp−v) between a highest portion and a lowest portion of the surface of the single fiber is 5 to 25 nm, and in which an average roughness Ra is 2 to 6 nm, and each of which has a ratio of 1.00 to 1.01 of a major axis to a minor axis (major axis/minor axis) of a cross-section of the single fiber; wherein a mass of the single fiber per unit length falls within the range of 0.030 to 0.042 mg/m; a strand strength is 5900 MPa or more; a strand elastic modulus measured by the ASTM method is 250 to 380 GPa; and a knot tenacity is 900 N/mm^2 or more.

3. The carbon fiber bundle according to claim **1** or **2**, wherein a hemispherical defect having a size within a predetermined range is formed on a single fiber surface by a laser, the fiber is broken at the hemispherical defective site by a tensile test, and "surface energy of surface formed by fracture" obtained from breaking strength of the fiber and the size of the hemispherical defect in accordance with the Griffith Equation (1) is 30 N/m or more, wherein σ is a breaking strength; E is an ultrasonic elastic modulus of a carbon fiber bundle; and C is a size of a hemispherical defect.

$$\sigma=(2E/\pi C)^{1/2}\times(\text{surface energy of surface formed by fracture})^{1/2} \quad (1)$$

4. The carbon fiber bundle according to any of claims **1** to **3**, wherein an ipa value obtained by an electrochemical measuring method (cyclic voltammetry) is 0.05 to 0.25 $\mu A/cm^2$, and an amount of an oxygen-containing functional group (O1S/C1S) in a carbon fiber surface obtained by X-ray photoelectron spectroscopy falls within the range of 0.05 to 0.15.

5. The carbon fiber bundle according to any of claims **1** to **4**, wherein a Si amount measured by ICP emission spectrometry is 200 ppm or less.

6. The carbon fiber bundle according to any of claims **1** to **5**, sized by a sizing agent composition comprising a urethane modified epoxy resin, which is a reaction product of (a) an epoxy resin having a hydroxy group, (b) a polyhydroxy compound and (c) a diisocyanate containing an aromatic ring, or sized by a sizing agent composition comprising a mixture of the urethane modified epoxy resin and (a) an epoxy resin having a hydroxy group and/or (d) an epoxy resin having no hydroxy group.

7. The carbon fiber bundle according to claim **6**, wherein (a) the epoxy resin having a hydroxy group is a bisphenol type epoxy resin.

8. The carbon fiber bundle according to claim **6** or **7**, wherein (b) the polyhydroxy compound is any one from among an adduct of a bisphenol-A with an alkylene oxide, an aliphatic polyhydroxy compound and a polyhydroxy monocarboxy compound or a mixture thereof.

9. The carbon fiber bundle according to any of claims **6** to **8**, wherein (c) the diisocyanate containing an aromatic ring is toluene diisocyanate or xylene diisocyanate.

10. The carbon fiber bundle according to any of claims **1** to **9**, wherein a total content of metals including an alkaline metal, an alkaline earth metal, zinc, iron and aluminum is 50 ppm or less.

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