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

(11) **EP 4 403 680 A1**

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

(43) Date of publication:
24.07.2024 Bulletin 2024/30

(21) Application number: **22869744.7**

(22) Date of filing: **18.08.2022**

(51) International Patent Classification (IPC):
D01F 9/22 *(2006.01)* ***D01F 6/18*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
D01F 6/18; D01F 9/22

(86) International application number:
PCT/JP2022/031179

(87) International publication number:
WO 2023/042597 (23.03.2023 Gazette 2023/12)

(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

(30) Priority: **15.09.2021 JP 2021149992**

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

(72) Inventors:
- **SUGA, Yuki**
  Iyo-gun, Ehime 791-3193 (JP)
- **TANAKA, Fumihiko**
  Iyo-gun, Ehime 791-3193 (JP)
- **WATANABE, Jun**
  Iyo-gun, Ehime 791-3193 (JP)

(74) Representative: **Kador & Partner Part mbB**
Corneliusstraße 15
80469 München (DE)

(54) CARBON FIBER BUNDLE AND PRODUCTION METHOD THEREFOR

(57) According to the present invention, a carbon fiber composite material, which has excellent energy absorption and is composed of a carbon fiber having high strength and high elongation, is provided by a production method yielding an excellent production amount. This carbon fiber bundle having a plurality of single fibers has a strand elastic modulus of 260-350 GPa, a strength of 6.5-8.5 GPa, an elongation of at least 1.8%, a filament number of 1,000-9,000, and a total fineness of 0.15-0.35 g/m, wherein the average value of major axis/minor axis ratios in single fiber cross sections is 1.01-1.08, the coefficient of variation is 1-4%, and the skewness is 0.3-1.2.

EP 4 403 680 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a carbon fiber bundle that is suitable for producing fabrics that are high in formability while having good characteristics for forming carbon fiber composite materials with enhanced energy absorption performance and also relates to a method for the production thereof.

BACKGROUND ART

[0002] Polyacrylonitrile based carbon fiber bundles (hereafter, carbon fiber bundles refer to polyacrylonitrile based carbon fiber bundles unless specifically described otherwise) are lightweight material with high strength and high elastic modulus and can serve as an important item for producing lightweight components. As a reinforcing base for the production of carbon fiber reinforced plastics (hereinafter occasionally abbreviated as CFRPs), reinforcing fabrics that are produced by processing carbon fiber bundles into fabrics have been used frequently in order to ensure both good mechanical characteristics and high formability. With excellent properties, CFRPs that incorporate such reinforcing bases have been employed in structural materials for automobiles, aircraft, etc., and are now required to have further enhanced tensile strength and impact energy absorption performance (hereinafter occasionally referred to as impact resistance).

[0003] Carbon fiber fabrics include carbon fiber bundles of carbon fiber filaments gathered together. Therefore, since these carbon fiber bundles have elliptical cross sections, when they are in a woven state, particularly in the case of conventionally known bidirectional fabrics, therefore, the adoption of a plain weave structure is advantageous because each of the weft yarns alternately run above and below the warp yarns while forming many crossing points to ensure a stable structure, although they are disadvantageous in that large crimps are likely to occur at the crossing points where warp yarns and weft yarns intersect with each other. In particular, this tendency increases in the case of fabrics containing carbon fiber bundles with a larger overall fineness because carbon fiber bundles with large thickness are interlaced with each other in them. In the case of fabrics with large crimps, carbon fiber bundles cannot show full performance because when stress is applied to the CFRPs, it tends to concentrate at the crossing points where crimps exist. Thus, it cannot be said that CFRPs including such fabrics can always have sufficiently large elongation percentage.

[0004] Apart from this, there are unidirectional and multidirectional structures as fabric structures that are formed of carbon fiber bundles, and attempts have been made to reduce or avoid the formation of crimps by adopting such weave structures as twill weaves. However, none of these attempts can be said to have been successful in allowing carbon fiber bundles to fully express the excellent resin impregnated strand strength (hereinafter occasionally referred to simply as strand strength) inherent therein, and currently, the formation of crimps is inevitable in fabric structures. Therefore, although an improvement in carbon fiber bundles has a larger effect than an improvement in the fabric structures, it has been impossible to produce CFRPs that have a satisfactorily high overall impact resistance because the carbon fiber bundles present in fabrics are low in elongation percentage.

[0005] As an attempt aiming to reduce the crimp angle in fabrics, Patent document 1 adopts the application of carbon fiber bundles with a thickness of 0.09 mm or less and an areal weight of 85 g/m^2 or less. These carbon fiber bundles are so thin, wide, and flattened that the carbon fiber bundles have smaller crimps and can work effectively in realizing reinforcing effects in thin CFRPs.

[0006] As an attempt aiming to enhance the strand strength and elongation percentage of the carbon fiber bundles themselves, Patent document 2 proposes to increase the fracture toughness, which serves to achieve a maximum strand strength of 8.4 GPa and a resin impregnated strand elastic modulus (hereinafter occasionally referred to as strand elastic modulus) of 325 GPa (Example 3). In Patent document 3 as well, the fracture toughness of carbon fiber is increased to realize a maximum strand strength of 7.9 GPa and a strand elastic modulus of 350 GPa (Example 7). As for the cross sectional shape of carbon fiber bundles, Patent document 4 proposes the technique of twisting the carbon fiber bundles during the flame resistant treatment step, which serves to provide carbon fiber bundles having flattened cross sections. Patent document 5 proposes the technique of mixing carbon fibers with different cross sectional shapes and twisting these carbon fiber bundles with the aim of allowing the carbon fiber filaments to have an increased skewness of the long diameter to short diameter ratio. This serves successfully to produce carbon fiber bundles having flattened cross sections while maintaining the strand strength of the carbon fiber bundles at a certain constant level.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0007]

[Patent document 1] Japanese Unexamined Patent Publication (Kokai) No. SHO-58-191244
[Patent document 2] Japanese Unexamined Patent Publication (Kokai) No. 2017-137614
[Patent document 3] International Publication WO 2016/68034
[Patent document 4] Japanese Unexamined Patent Publication (Kokai) No. 2015-67910
[Patent document 5] Japanese Unexamined Patent Publication (Kokai) No. 2021-059829

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] These conventional technologies, however, have such problems as described below.

[0009] Patent document 1 proposes the use of thin carbon fiber bundles to achieve a high reinforcing effect for fabrics, but it only proposes a method for spreading carbon fiber bundles by feeding them into a flowing liquid and does not discuss the characteristics of the carbon fiber bundles, and as a result, it fails to provide carbon fiber bundles that have satisfactory levels of fiber spreading property and elongation percentage. Patent documents 2 and 3 propose methods to improve strand strength by increasing toughness, but they do not include a step for twisting the fibers in the flame resistant treatment step, and accordingly, the cross sections of the filaments are not controlled properly, leading to carbon fiber bundles that are excessively large and thick. Even when the carbon fiber bundles are split in half to decrease the bundle width, it fails to produce filaments that have cross sectional shapes required to allow the bundles to have smaller thickness. Patent document 4 proposes to perform twisting in the flame resistant treatment step to provide carbon fiber bundles with highly flattened cross sections, but since it does not focus on elongation improvement to be achieved by improving the strand strength or strand elastic modulus, the maximum strand strength of the bundles produced in Examples is as low as 5.6 GPa and their elongation percentage is low as well. Patent document 5 proposes the technique of mixing carbon fibers with different cross sectional shapes and twisting them in order to increase the skewness of the filament cross sectional shape and the degree of flattening of the carbon fiber bundle cross section. However, it does not focus on elongation percentage. The maximum strand strength reached in Examples is as low as 4.8 GPa (Example 7) and the strand elastic modulus is as low as 317 GPa, failing to realize a satisfactory degree of elongation percentage. As described above, although various attempts have been made separately so far aiming to provide carbon fiber bundles with improved strand strength and elongation percentage and to identify a good filament cross sectional shape that serves to provide carbon fiber bundles with an improved degree of flattening, not only they have different effects, but also it is difficult to find a good combination among the proposed operations because those designed to increase their degree of flattening tend to work to reduce their strand strength. Accordingly, there have been no studies focusing on their combination.

[0010] Thus, the present invention aims to provide carbon fiber bundles that are high in strand strength to suit fabric production from the carbon fiber bundles, high in elongation percentage to achieve high impact resistance, low in the overall fineness to realize small crimps, high in the degree of flattening of carbon fiber bundles, and also high in their skewness.

MEANS OF SOLVING THE PROBLEMS

[0011] To achieve the aforementioned object, the present invention provides a carbon fiber bundle that includes a plurality of filaments and is characterized by having a strand elastic modulus of 260 to 350 GPa, a strand strength of 6.0 to 8.5 GPa, an elongation percentage of 1.8% or more, a filament count of 1,000 to 9,000, and an overall fineness of 0.15 to 0.35 g/m, wherein the long diameter to short diameter ratios of the filament cross sections have an average value of 1.01 to 1.08, a coefficient of variation of 1% to 4%, and a skewness of 0.3 to 1.2.

EFFECT OF THE INVENTION

[0012] The carbon fiber bundle according to the present invention is high in strand strength and also high in elongation percentage and, due to a small overall fineness of the carbon fiber bundle and a large skewness of the carbon fiber filaments, the carbon fiber bundle can possess a thin cross section. As a result, CFRP materials produced by using fabrics made of such carbon fiber bundles tend to be very high in energy absorption capability.

[Brief description of the drawings]

[0013] [Fig. 1] This is a diagram of a typical cross section of a carbon fiber bundle.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0014] For the present invention, the filament cross sections thereof have an average long diameter to short diameter ratio of 1.01 to 1.08, preferably 1.01 to 1.05, and more preferably 1.01 to 1.03. For the present invention, the long diameter to short diameter ratio of a filament cross section is the ratio calculated by dividing the long diameter by the short diameter. Furthermore, for the present invention, the term "filament cross section" refers to a cross section of a filament that is perpendicular to the fiber axis. In addition, for the present invention, the term "long diameter" refers to the maximum Feret diameter, i.e. the length of the longer side of the rectangle that is inscribed around the filament cross section, while the term "short diameter" refers to the minor axis of an ellipse that has a major axis equal to the aforementioned long diameter and has the same cross sectional area as the filament cross section. The term "average" means an arithmetic average value calculated without weighting, and an average long diameter to short diameter ratio closer to 1.00 indicates that there exist a larger number of filaments having nearly circular cross sections. As the average long diameter to short diameter ratio increases, the carbon fiber bundle tends to decrease in elongation percentage, and accordingly, the average long diameter to short diameter ratio should preferably be 1.01 or more. A good carbon fiber bundle can be maintained without suffering a significant decrease in elongation percentage when the average long diameter to short diameter ratio is 1.08 or less. To control the average long diameter to short diameter ratio of the filament cross section in the aforementioned range, a generally known method is by adjusting the coagulation bath conditions.

[0015] For the present invention, it is preferable that the proportion of filaments with long diameter to short diameter ratios of 1.00 to 1.03 be 30% to 90%, more preferably 40% to 85%, and still more preferably 50% to 80%. A larger long diameter to short diameter ratio tends to lead to better fiber spreading property, but if the proportion of filaments with long diameter to short diameter ratios of 1.00 to 1.03 is more than 90%, it may cause a decrease in strand strength. Both of these characteristic values can be maintained more easily at high levels if filaments with long diameter to short diameter ratios of 1.00 to 1.03 account for 30% or more. Filaments with long diameter to short diameter ratios of 1.00 to 1.03 can be obtained by, for example, adjusting the coagulation conditions appropriately or controlling the force applied perpendicular to the fiber axis to squeeze the filaments.

[0016] For the present invention, it is preferable that the proportion of filaments with long diameter to short diameter ratios of 1.04 to 1.10 be 10% to 40%, more preferably 15% to 25%. A higher long diameter to short diameter ratio tends to lead to better fiber spreading property, but if the proportion of filaments with long diameter to short diameter ratios of 1.04 to 1.10 is more than 40%, it may cause a decrease in strand strength. Both of these characteristic values can be maintained more easily at high levels if filaments with long diameter to short diameter ratios of 1.04 to 1.10 account for 10% or more. Filaments with long diameter to short diameter ratios of 1.04 to 1.10 can be obtained by, for example, adjusting the coagulation conditions appropriately or controlling the force applied perpendicular to the fiber axis to squeeze the filaments.

[0017] For the present invention, the coefficient of variation in the long diameter to short diameter ratio of the filaments is 1% to 4%, preferably 1% to 3%, and more preferably 1% to 2%. According to the general definition, the coefficient of variation is calculated by dividing the standard deviation by the average value and multiplying the quotient by 100. A larger coefficient of variation in the long diameter to short diameter ratio indicates a wider distribution of long diameter to short diameter ratios and this has relations with the fiber spreading property of the carbon fiber bundle, which serves as an indicator of how easily the cross section of the carbon fiber bundle can be flattened. A coefficient of variation of 1% or more indicates good fiber spreading property for the carbon fiber bundle while if it is 4% or less, the carbon fiber bundle is prevented from suffering a significant decrease in elongation percentage. Useful methods to allow the coefficient of variation in long diameter to short diameter ratios of a filament cross section to be controlled in the aforementioned range will be described later.

[0018] For the present invention, it is preferable that the skewness of the long diameter to short diameter ratio of the filaments be 0.3 to 1.2, preferably 0.3 to 1.1, more preferably 0.4 to 1.0, and still more preferably 0.6 to 1.0. Skewness is a parameter that represents the degree of asymmetry of a distribution and is defined by the following formula (1):

$$\text{Skewness} = n / ((n-1) \times (n-2)) \times \Sigma\{(xi-\langle x\rangle)/s\}^3 \qquad (1)$$

[0019] Here, n is the number of filaments (number); xi is the long diameter to short diameter ratio (-) of the i-th filament; <x> is the average long diameter to short diameter ratio (-); and s is the standard deviation (-) of the long diameter to short diameter ratio. Furthermore, Σ means summation over all n's. i.e. the numbers of filaments. For the frequency distribution of any parameter of interest, a skewness of 0 indicates a symmetric distribution, while a negative skewness indicates a distribution broader toward the smaller side and a positive skewness indicates a distribution broader toward the larger side.

[0020] To realize a decrease in crimp angle required in a fabric, it is necessary to flatten the cross section of the carbon fiber bundles. However, merely increasing the average long diameter to short diameter ratio or controlling the coefficient

of variation in the long diameter to short diameter ratios of the carbon fiber filaments can lead to an undesirable decrease in the elongation percentage of the carbon fiber bundles, and it was found that controlling the skewness within the aforementioned range is important to produce a carbon fiber bundle that has a high elongation percentage and good fiber spreading property simultaneously.

[0021] By definition, a large skewness of the long diameter to short diameter ratio means a state in which the average long diameter to short diameter ratio is maintained at a low level although there exists a certain volume of filaments with large long diameter to short diameter ratios. Smaller long diameter to short diameter ratios allow the carbon fiber bundle to have a higher elongation percentage, while larger long diameter to short diameter ratios allows the carbon fiber bundle to have better fiber spreading property. The balance relating to the fiber spreading property of the carbon fiber bundle is thought to be strongly influenced by the proportions of filaments with different long diameter to short diameter ratios. The effect caused by filaments with large long diameter to short diameter ratios in increasing the fiber spreading property of the carbon fiber bundle must be relatively greater than the effect caused by filaments with small long diameter to short diameter ratios in reducing the elongation percentage of the carbon fiber bundle, and accordingly, it is considered that the addition of a small volume of filaments with large long diameter to short diameter ratios is important to maximize the effect for increasing the fiber spreading property of the carbon fiber bundle without causing a significant decrease in its elongation percentage.

[0022] Improvements in both of them can be achieved simultaneously at a high level when the skewness of the long diameter to short diameter ratio is 0.3 or more. An elongation percentage in a desired range can be realized when the skewness of the long diameter to short diameter ratio is 1.2 or less. For the present invention, in order to control the coefficient of variation and skewness of the long diameter to short diameter ratio within the aforementioned ranges, a good controlling method is to twist the flame resistant treated fibers and apply tension so that pressing forces are generated between filaments to cause their deformation. Fine adjustments are made based on observations of cross sections of resulting carbon fiber filaments, thus preparing the carbon fiber bundle according to the present invention that meets the specified numerical requirements.

[0023] The carbon fiber bundle according to the present invention has a filament count of 1,000 to 9,000. The filament count is defined as the number of filaments contained in a carbon fiber bundle. A filament count of 1,000 or more ensures a sufficient elongation percentage, while a filament count of 9,000 or less makes it possible to maintain a small overall fineness and ensure a crimp angle suitable for fabric production. An appropriate filament count can be set in the manufacturing process for the polyacrylonitrile based carbon fiber precursor fiber bundle.

[0024] The carbon fiber bundle according to the present invention has an overall fineness of 0.15 to 0.35 g/m, preferably 0.20 to 0.30 g/m. The overall fineness of a carbon fiber bundle is defined as its mass per meter. It is related with the filament diameter and the filament count of the carbon fiber bundle, and a smaller overall fineness leads to a smaller crimp angle. A CFRP material with a high impact resistance can be produced when the overall fineness is 0.15 g/m or more, while a crimp angle suitable for fabric production can be realized when it is 0.35 g/m or less. The overall fineness can be determined by measuring the length of the carbon fiber bundle and its mass for that length. The overall fineness can be controlled by adjusting the filament count, apart from changing the filament diameter. However, since a decrease in the filament count is likely to cause a decline in the elongation percentage of the carbon fiber bundle, and accordingly, the same characteristics tend not to be maintained when simply changing the filament count.

[0025] The carbon fiber bundle according to the present invention has a strand elastic modulus of 260 to 350 GPa, preferably 270 to 320 GPa, and more preferably 270 to 300 GPa. The strand elastic modulus of a carbon fiber bundle is an indicator of the resistance to deformation when it is under load, or in other words, it serves as an indicator of the lightness of the material. The strand elastic modulus of a carbon fiber bundle can be determined according to the tensile test of resin impregnated strands specified in JIS R7608:2004. A carbon fiber bundle gives a nonlinear stress-strain curve that is convex downward, but the strain range is generally limited to 0.1% to 0.6%, and a strand elastic modulus in this strain range is used. If the strand elastic modulus is 260 GPa or more, it indicates that the carbon fiber bundle is high in lightness, whereas if the strand elastic modulus is 350 GPa or less, a high elongation percentage can be realized in comparison to the strength to be achieved, thus ensuring a sufficient impact resistance. The strand elastic modulus can be controlled by adjusting various conditions in the carbonization step, such as maximum temperature, duration of heat treatment at the maximum temperature, temperature increasing rate, and stretching ratio.

[0026] The carbon fiber bundle according to the present invention has a strand strength of 6.0 to 8.5 GPa, preferably 6.5 to 8.0 GPa, and more preferably 7.0 to 8.0 GPa. The strand strength of a carbon fiber bundle is an indicator of the resistance to breakage when it is under load. The strand strength of a carbon fiber bundle can be determined according to the tensile test of resin impregnated strands specified in JIS R7608:2004. If the strand strength is 6.0 GPa or more, it ensures a sufficient impact resistance. There are no specific limitations on the upper limit of the strand strength, but a fully satisfactory impact resistance is likely to be achieved if it is at least 8.5 GPa. Strand strength can be increased by controlling various conditions including flame resistant treatment conditions and carbonization conditions, such as by improving defect suppression and fracture toughness enhancement.

[0027] The carbon fiber bundle according to the present invention has an elongation percentage of 1.8% or more,

preferably 2.0% or more, more preferably 2.2% or more, and still more preferably 2.4% or more. The elongation percentage of a carbon fiber bundle can be determined according to the tensile test of resin impregnated strands specified in JIS R7608:2004. The elongation percentage of a carbon fiber bundle is difficult to measure because it gives a nonlinear stress-strain curve. In this tensile test, however, elongation percentage is calculated by dividing the aforementioned strand strength by the aforementioned strand elastic modulus. If the elongation percentage is 1.8% or more, it ensures a sufficient impact resistance. There are no specific limitations on the upper limit of the elongation percentage, but a satisfactory impact resistance is ensured in most cases if it is at least 3.0%. The elongation percentage of a carbon fiber bundle can be adjusted appropriately by controlling the strand strength and strand elastic modulus to maintain them in a good balance.

[0028] The cross sectional shape of a carbon fiber bundle is preferably such that the area ratio calculated by dividing the cross sectional area of the carbon fiber bundle by the area of the rectangle that is defined later (area ratio of carbon fiber bundle's cross section) is 0.50 to 0.70, more preferably 0.60 to 0.70. If the area ratio is 0.78, it theoretically means that the cross section is elliptical in comparison with the defined rectangle, whereas if the area ratio is 0.78 or less, the cross section of the carbon fiber bundle has a concavity, that is, there are concavities in some part of the filaments present in the carbon fiber bundle. If it is 0.70 or less, as the effect of feeding a plurality of fiber bundles to one groove, they partially contain filaments with concavities, thus allowing the carbon fiber bundle to have a flattened cross section, and as a result, this facilitates the production of a fabric formed of carbon fiber bundles with a desirable degree of flattening. If it is 0.50 or more, it serves to prevent the filaments present in the carbon fiber bundle from being deformed excessively and accordingly, this ensures that the carbon fiber bundle has a desirable strand strength. The cross sectional shape of a carbon fiber bundle is influenced by such factors as the tension and twist angle in the flame resistant treatment step, but the partial concavities in the carbon fiber bundle can be controlled mainly by feeding a plurality of fiber bundles to a single groove in the flame resistant treatment step and allowing them to come in contact with each other.

[0029] A method for producing the carbon fiber bundle according to the present invention is described below.

[0030] For the production of a polyacrylonitrile based carbon fiber precursor fiber bundle (hereinafter occasionally referred to as precursor fiber bundle), it is preferable to use a polyacrylonitrile based polymer as raw material. For the present invention, it is preferable that the polyacrylonitrile based polymer be a polymer material in which acrylonitrile accounts for 90 to 100 mol%. For the production of a precursor fiber bundle, it is preferable for the polyacrylonitrile based polymer to contain a copolymer component in order to ensure an improved strand strength. From the viewpoint of promoting the flame resistant treatment, examples of monomers that can be used as copolymer components include those containing at least one carboxylic acid group or one amide group.

[0031] For the production of a precursor fiber bundle, either the dry-wet spinning technique or the wet spinning technique may be used as yarn-making method, but the use of the dry-wet spinning is preferable because it is advantageous for producing a carbon fiber bundle having a desired strand strength.

[0032] The yarn-making process preferably includes a spinning step in which the dry-wet spinning technique is performed to spin a yarn by discharging a spinning dope solution through a spinning spinneret into a coagulating bath, a rinsing step in which the fiber bundle resulting from the spinning step is stretched while being rinsed in a water bath, and a dry heat treatment step in which the fiber bundle resulting from the rinsing step is treated in dry heat, and may also include a steam stretching step, as required, in which the fiber bundle resulting from the dry heat treatment step is subjected to steam stretching. Here, the order of the steps may be rearranged as appropriate. The spinning dope solution is prepared by dissolving the aforementioned polyacrylonitrile based polymer in a solvent such as dimethyl sulfoxide, dimethyl formamide, and dimethyl acetamide that can dissolve polyacrylonitrile.

[0033] It is preferable for the aforementioned coagulation bath to contain both the same solvent as used in the spinning dope solution, such as dimethyl sulfoxide, dimethyl formamide, and dimethyl acetamide, and a so-called coagulation accelerating agent. The coagulation accelerating agent to use may be one that is not able to dissolve the aforementioned polyacrylonitrile based polymer and is compatible with the solvent present in the spinning dope solution. Specifically, it is preferable to adopt water as the coagulation accelerating agent. It has been known that the cross sectional shape is likely to change here depending on the coagulation conditions. Specifically, a circular cross section is formed when the solvent concentration in the coagulation bath is either as low as 40 mass% or less or as high as around 80 mass%, while a β-type cross section is formed when the concentration is in an intermediate range.

[0034] For the rinsing bath used in the aforementioned rinsing step, it is preferable to adopt a multiple stage type rinsing bath controlled at temperatures in the range of 30°C to 98°C. Here, the stretching ratio used in the rinsing step is preferably 2 to 6. Subsequently, it is preferable to apply an oil agent, such as silicone based one, to the fiber for the purpose of improving the strand strength. Such a silicone based oil agent preferably contains an amino-modified silicone.

[0035] For the dry heat treatment step, a generally known method may be used. For example, the drying temperature may be in the range of 100°C to 200°C.

[0036] After carrying out the aforementioned rinsing step and dry heat treatment step, steam stretching is performed if required, thereby providing a precursor fiber bundle that is suitable for producing the carbon fiber bundle according to the present invention. It is preferable for the steam stretching to be carried out in pressurized steam to a stretching ratio

of 2 to 6.

[0037] In the process for the production of a carbon fiber bundle, the precursor fiber bundle is subjected to a flame resistant treatment step, a preliminary carbonization step, and a carbonization step, thereby providing a carbon fiber bundle. In particular, in order to obtain a carbon fiber bundle with an increased strand strength, it is preferable, particularly in the case where a precursor fiber bundle is subjected to the flame resistant treatment step, that the treatment be controlled in such a manner that the resulting resistant treated fiber bundle will give an infrared spectrum in which the ratio of the peak intensity at 1,453 cm^{-1} to the peak intensity at 1,370 cm^{-1} is in the range of 0.70 to 0.75 while at the same time the ratio of the peak intensity at 1,254 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum is in the range of 0.50 to 0.65. The peak at 1,453 cm^{-1} in the infrared spectrum is attributed to alkene and its intensity decreases with the progression of the flame resistant treatment. The peaks at 1,370 cm^{-1} and 1,254 cm^{-1} are attributed to the flame resistant treated structure and their intensities increase with the progression of the flame resistant treatment. In the case where the resulting flame resistant treated fiber has a specific gravity of 1.35, it is preferable that the ratio of the peak intensity at 1,453 cm^{-1} to the peak intensity at 1,370 cm^{-1} be about 0.63 to 0.69. In addition, it is preferable for the flame resistant treatment conditions to be set up in such a manner that the ratio of the peak intensity at 1,254 cm^{-1} to the peak intensity at 1,370 cm^{-1} is to be 0.50 to 0.65. This peak intensity ratio decreases with the progression of the flame resistant treatment, and in particular, a large decrease occurs in initial stages. Depending on the flame resistant treatment conditions, however, the peak intensity ratio may not decrease to 0.65 or less even when the treatment is performed for a prolonged time.

[0038] To allow both of these peak intensity ratios to be in the desired ranges, basically the treatment conditions are set up focusing mainly on the facts that the copolymer component accounts for only a small proportion in the polyacrylonitrile based polymer present in the precursor fiber bundle, that the precursor fiber bundle has a high degree of crystal orientation, that the precursor fiber bundle should have a decreased filament fineness, and that the flame resistant treatment temperature should be increased in the latter half of the step.

[0039] It is preferable that the polyacrylonitrile based carbon fiber precursor fiber bundle be subjected to flame resistant treatment performed for 8 to 25 minutes until the ratio of the peak intensity at 1,453 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum comes into the range of 0.98 to 1.10 (first flame resistant treatment step), followed by additional flame resistant treatment performed for 5 to 20 minutes until the ratio of the peak intensity at 1,453 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum comes into the range of 0.70 to 0.75 while at the same time the ratio of the peak intensity at 1,254 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum comes into the range of 0.50 to 0.65 (second flame resistant treatment step). To shorten the flame resistant treatment time in the second flame resistant treatment step, the adjustment of the flame resistant treatment temperature to a high value may be effective, but the optimum flame resistant treatment temperature depends on the characteristics of the precursor fiber bundle. The adjustment of the flame resistant treatment temperature preferably to 260°C to 290°C is favorable to realize control in the aforementioned infrared spectrum ranges. The flame resistant treatment temperature does not need to be constant and may be set in multiple temperature stages. To obtain a carbon fiber bundle having an increased strand strength, it is preferable to set a higher flame resistant treatment temperature and a shorter flame resistant treatment time. In the first flame resistant treatment step, it is preferable to perform the treatment for a flame resistant treatment time of 10 to 25 minutes at a flame resistant treatment temperature that allows the ratios to come in the aforementioned ranges.

[0040] The flame resistant treatment time mentioned herein refers to the time period over which the fiber stays in the flame resistant treatment furnace, and the flame resistant treated fiber bundle refers to the fiber bundle that has resulted from the flame resistant treatment step and is not yet subjected to the preliminary carbonization step. In addition, the peak intensity mentioned herein refers to the absorbance at a particular wavelength determined by sampling a small amount of a flame resistant treated fiber bundle, subjecting it to infrared spectrum analysis, and applying baseline correction to the spectrum obtained, with peak splitting etc. remaining unamended. Here, the concentration of the sample is diluted to 0.67 mass% with KBr before measurement. Each time the flame resistant treatment conditions are changed, the infrared spectrum should be measured in this way and used for examination of the conditions. If the infrared spectrum peak intensity ratios of a flame resistant treated fiber bundle are controlled appropriately, it allows the resulting carbon fiber bundle to have an appropriately adjusted strand strength.

[0041] For the present invention, the flame resistant treatment step refers to a step for heat-treating a precursor fiber bundle in an oxygen-containing atmosphere at 200°C to 300°C.

[0042] For the flame resistant treatment step, it is preferable to set an appropriate total treatment time in the range of 15 to 40 minutes. In addition, for the purpose of obtaining a carbon fiber bundle with an improved strand strength, the treatment time for the flame resistant treatment step is set preferably in such a manner that the resulting flame resistant treated fiber has a specific gravity of 1.28 to 1.32. A more preferable treatment time for the flame resistant treatment step may be found depending on the flame resistant treatment temperature. If the specific gravity of the flame resistant treated fiber bundle fails to be 1.28 or more, the strand strength of the carbon fiber bundle can be lower than desired in some cases. If the specific gravity of the flame resistant treated fiber bundle is 1.32 or less, it can ensure an increased

strand strength. The specific gravity of the flame resistant treated fiber bundle can be controlled by changing the flame resistant treatment time and the flame resistant treatment temperature used in the flame resistant treatment step. In addition, the switching from the first flame resistant treatment step to the second flame resistant treatment step is implemented preferably at a time point at which the specific gravity of the fiber bundle is in the range of 1.21 to 1.23. Even in doing this, adjusting the aforementioned infrared spectrum intensity ratios to values in the specified ranges should be prioritized in controlling the conditions for the flame resistant treatment step. The preferable ranges of the flame resistant treatment time and flame resistant treatment temperature can vary depending on the characteristics of the precursor fiber bundle and the copolymer composition of the polyacrylonitrile based polymer.

[0043] The twisting treatment designed to adjust the skewness is performed in this second flame resistant treatment step, in which the twist angle of the fiber bundle is preferably maintained at 0.2° or more during the flame resistant treatment. For the present invention, the twist angle during the flame resistant treatment is calculated by the following formula from the weight per meter (y) (g/m) of the precursor fiber bundle, its density (d) (g/cm^3), and twist count (T) (turns/m).

$$\text{twist angle (°)} = \arctan\{(0.01 \times y / (\pi \times d))^{0.5} \times 10^{-6} \times \pi \times T\}$$

[0044] To add a twist to the fiber under the flame resistant treatment, an appropriate method may be selected from generally known ones. Specifically, twisting can be controlled by a method in which a precursor fiber bundle is first wound up on a bobbin, followed by unwinding the fiber bundle with the bobbin being rotated in the plane perpendicular to the direction of the unwinding direction or by a method in which, instead of winding up on a bobbin, the traveling fiber bundle is brought into contact with rotating rollers, belts, etc., to give a twist. A larger twist angle can work more effectively in improving the degree of flattening of the carbon fiber bundle, but a sufficient effect can be achieved when the twist angle is 0.2° or more.

[0045] While adding a twist in the second flame resistant treatment step, it is preferable for the tension on the fiber bundle under the flame resistant treatment to be maintained at 0.7 to 1.5 mN/dtex. The tension maintained in the flame resistant treatment step is calculated by dividing the tension (mN) measured at the inlet of the flame resistant treatment furnace by the overall fineness (dtex), which is the product of the filament fineness (dtex) multiplied by the filament count of the precursor fiber bundle in use. If the tension is maintained in this numerical range, it makes it easier to impart concavities to the carbon fiber filaments.

[0046] Then, in the second flame resistant treatment step, a plurality of fiber bundles is fed to a groove on a roller, in which they are subjected to flame resistant treatment. This serves to allow the overall tension on the plurality of fiber bundles present in a groove to be increased while maintaining a low tension on each individual flame resistant treated fiber bundle. Accordingly, stress is applied to some filaments on the roller in the perpendicular direction to their cross sections, making it easier to increase the long diameter to short diameter ratios of the filament cross sections. This method for applying tension makes it possible to control the cross sectional shapes of part of the filaments while maintaining the overall cross sectional shape. Here, the term "a plurality" preferably means 2 to 6, more preferably 3 to 5.

[0047] In the preliminary carbonization step, which is designed to perform preliminary carbonization, the fiber bundles resulting from the aforementioned first and second flame resistant treatment steps are subjected to heat treatment in an inactive atmosphere at a maximum temperature of 500°C to 1,200°C until the specific gravity preferably reaches 1.5 to 1.8. In the preliminary carbonization step, the stretching ratio is maintained preferably at 1.00 to 1.20. If the stretching ratio in the preliminary carbonization step is 1.00 or more, it is likely to lead to a higher strand elastic modulus and make it easier to increase the strand strength. If the stretching ratio in the preliminary carbonization step is 1.20 or less, it makes it easier to control the strand elastic modulus at 350 GPa or less.

[0048] The preliminarily carbonized fiber bundle is then carbonized in an inert atmosphere preferably at a maximum temperature of 1,000°C to 1,500°C, more preferably at a maximum temperature of 1,000°C to 1,200°C. In order to obtain a carbon fiber bundle having a higher elongation percentage, it is preferable for the maximum temperature in the carbonization step to be as low as possible, but the strand strength is likely to decrease if it is too low. Therefore, it is preferable to set an appropriate temperature in consideration of the balance between these factors.

[0049] Furthermore, in the carbonization step, it is preferable for treatment at the maximum temperature to be continued for 20 to 60 seconds. A shorter treatment time at the maximum temperature serves to allow the strand elastic modulus to be controlled at a lower value, and accordingly, the treatment time is preferably 60 seconds or less while a treatment time of 20 seconds or more makes it possible to achieve a stable strand elastic modulus.

[0050] The heating rate used in the carbonization step is preferably 0.40°C/sec to 1.10°C/sec, more preferably 0.40°C/sec to 0.60°C/sec. The heating rate used in the carbonization step influences the outgassing rate of decomposition gases, hence affecting the strand strength. For the present invention, the heating rate is defined as the average temperature increase speed (°C/sec) as the fiber passes through the region where the temperature is 1,000°C to 1,100°C. The temperature in the carbonization step is generally controlled by setting appropriate temperatures on the heaters,

and therefore, the heating rate is calculated based on the temperatures at the centers of the positions where the heaters are installed and the timing of the fiber passing there. If the heating rate is 0.40°C/sec or more, it serves to achieve a desired strand elastic modulus stably, whereas if it is 1.10°C/sec or less, it serves to prevent a decrease in the strand strength.

[0051] The carbon fiber bundle obtained as described above is preferably subjected to oxidation treatment to introduce an oxygen-containing functional group.

[0052] For the present invention, the fiber bundle resulting from the carbonization step described above is subjected to an electrolytic surface treatment to produce a carbon fiber bundle. Useful electrolytic surface treatment methods include gas phase oxidization, liquid phase oxidization, and liquid phase electrolytic oxidization, of which liquid phase electrolytic oxidization is preferably selected from the viewpoint of ensuring high productivity and uniform treatment. For the present invention, there are no specific limitations on the technique to use for liquid phase electrolytic oxidation and a generally known one may be selected appropriately.

[0053] Such electrolytic surface treatment may be followed by sizing treatment in order to allow the resulting carbon fiber bundle to develop bundling property. For the sizing, a sizing agent having a high compatibility with the matrix resin is selected appropriately depending on the type of the matrix resin to be adopted for the intended CFRP.

[0054] The carbon fiber bundle according to the present invention is preferably used mainly as weaving yarns for producing fabrics with crimps. In regard to their structures, they may be applied to unidirectional fabrics or multidirectional fabrics, but for the present invention, it is effective to apply the carbon fiber bundle as warp and weft to use for producing conventionally known types of bidirectional fabrics because the flattened cross section of the carbon fiber bundle serves for reducing crimps. In particular, its application to plain weave production is preferable because each of the weft yarns alternately run above and below the warp yarns while forming many crossing points to ensure a stable structure.

[0055] Reinforcing fabrics formed of such flattened, substantially untwisted carbon fiber bundles can maintain very small crimps at the crossing points of each carbon fiber bundle even when the fiber density is increased, thus serving to produce a CFRP with good elongation characteristics. Furthermore, each carbon fiber bundle maintains a flattened form in the fabric, allowing the fabric to be impregnated very efficiently with resin. As a result, a CFRP with uniform characteristics can be obtained, and desired elongation characteristics can be easily achieved. Here, the term "substantially untwisted" means a state in which the carbon fiber bundle has only one or less twist per meter. If the carbon fiber bundle is twisted, concavities and convexities are likely to occur in the twisted regions. As a result, when such bundles are woven into a fabric and subjected to external forces, stress concentrates in these twisted regions, leading to a CFRP having uneven elongation characteristics. The carbon fiber bundle according to the present invention can be used in an untwisted form.

[0056] A reinforcing fabric can be produced by the following method. Flattened, substantially untwisted carbon fiber bundles as described above are used as warp and/or weft yarns. To prevent the flattened shape of these carbon fiber bundles from being distorted and to prevent them from being twisted while they are unreeled, it is advisable to unreel the warp yarns perpendicularly to the bobbin's rotation axis and, if necessary, open and widen each weaving yarn during or after weaving. Such reinforcing fabrics can be used to produce preforms, prepregs, etc., that are to be molded into CFRPs, in which they can exhibit excellent properties as reinforcing bases. A preform can incorporate at least one sheet of any of the aforementioned reinforcing fabrics. Since it has only very small concavities and convexities, a preform using it shows very high formability in conforming to a mold, thus serving to produce a molded CFRP having a smooth surface. Reinforcing fabrics formed in this way can be used favorably in components that require good mechanical properties. It is advantageous to use these reinforcing fabrics as fabric prepregs for molding CFRPs or use them as fabric bases in vacuum forming processes.

[0057] In order to provide CFRPs having increased impact resistance, it is important for the carbon fiber bundle according to the present invention to be high in all of the following factors: strand elastic modulus, strand strength, elongation percentage, and overall fineness, as well as the average, coefficient of variation, and skewness of the long diameter to short diameter ratio.

[0058] The methods adopted for the present invention for the measurement of various physical properties are described below.

<Overall fineness>

[0059] From the carbon fiber bundle under examined, a sample with a length of 10 m is taken, dried at 120°C for 2 hours, and then weighed, followed by dividing the measured mass by 10 to determine the overall fineness, which is the mass per meter.

<Density>

[0060] The carbon fiber bundle under examination is dried first at 120°C for 2 hours. Using a dry type automatic density

meter, nitrogen as measuring medium, and a 10 cc type sample container, a sample with a volume adjusted to 3 to 6 cc is prepared. Three measurements should be taken and their average is adopted. Here, an AccuPyc 1330 dry type automatic density meter manufactured by Shimadzu Corporation was used for measurement.

<Strand strength, strand elastic modulus, and elongation percentage>

[0061] The strand strength, strand elastic modulus, and elongation percentage of a carbon fiber bundle are determined by the following procedures according to the test method for resin impregnated strands specified in JIS R7608:2004. A resin mixture consisting of Celloxide (registered trademark) 2021P (manufactured by Daicel Corporation), boron trifluoride monoethyl amine (manufactured by Tokyo Chemical Industry Co. Ltd.), and acetone mixed at a ratio of 100/3/4 (parts by mass) is prepared, and it is cured under the conditions of atmospheric pressure, a temperature of 125°C, and a curing time of 30 minutes. Seven carbon fiber strands are examined and measurements taken are averaged to represent their strand strength, strand elastic modulus, and elongation percentage. Here, the calculation of strand elastic modulus is based on measurements taken in the strain range of 0.1% to 0.6%.

<Twist angle in flame resistant treatment step>

[0062] The twist angle in the flame resistant treatment step is calculated by the following formula from the weight per meter (y) (g/m) of the precursor fiber bundle, its density (d) (g/cm^3), and twist count (T) (turns/m).

$$\text{Twist angle } (°) = \arctan\{(0.01 \times y / (\pi \times d))^{0.5} \times 10^{-6} \times \pi \times T\}$$

<Statistics of long diameter to short diameter ratio, coefficient of variation, and skewness>

[0063] There are no specific limitations on the evaluation methods to use for the long diameter to short diameter ratio, coefficient of variation, and skewness as long as they are evaluated according to the definitions given above, but for example, they can be evaluated as described below.

[0064] First, carbon fiber bundles are arranged in parallel and wrapped in a cylindrical shape using carbon tape. The bundle thus prepared is cut with scissors perpendicularly to the fiber axis to expose the filament cross sections. These filament cross sections are observed using a scanning electron microscope and their images are stored. The stored images are loaded into an open-source image analysis program (ImageJ (Version 1.53h)) and the contours of the filament cross sections are traced using the "Polygon selections" tool. In doing this, 20 to 100 points are used to draw the whole contour of one cross section. Then, the traced contour is retouched into a smooth curve using the "Fit spline" tool. After retouching, the points are moved slightly to better align the traced curve with the contour of the filament cross section. Then, the AR (aspect ratio) is calculated using the "Analyze particles" tool. Here, for the present invention, the aspect ratio refers to the long diameter to short diameter ratio. There are no specific limitations on the number of filaments as long as statistical bias is avoided. For example, the same procedure is carried out on 50 filaments. For this measurement, filaments should be selected evenly from different parts of the carbon fiber bundle. To calculate the proportion of filaments having a particular long diameter to short diameter ratio, the number of filaments having that long diameter to short diameter ratio is divided by the total number of filaments under examination and then multiplied by 100 (%). The average (-), coefficient of variation (%), and skewness (-) are calculated using the total number of filaments under examination. Here, the skewness of the long diameter to short diameter ratio is calculated according to the following formula (1).

$$\text{Skewness} = n / ((n-1) \times (n-2)) \times \Sigma\{(xi-\langle x\rangle)/s\}^3 \qquad (1)$$

[0065] Here, n is the number of filaments; xi is the long diameter to short diameter ratio (-) of the i-th filament; <x> is the average long diameter to short diameter ratio (-); and s is the standard deviation (-) of the long diameter to short diameter ratio. Furthermore, Σ means summation over all n's. i.e. the numbers of filaments. It is noted that the scanning electron microscope used in the Examples given below was a model S-4800 scanning electron microscope (SEM) manufactured by Hitachi High-Technologies Corporation and the observation was conducted at an acceleration voltage of 5 keV.

<Fiber spreading property>

[0066] Evaluation for the fiber spreading property is performed on a carbon fiber bundle with no sizing agent attached

thereon. If there is a sizing agent attached thereon, it is removed by burning it off in an oven or washing in a solvent before evaluation. A sample with a length of 2 cm is taken from the carbon fiber bundle and ensure it is in an untwisted state. The carbon fiber bundle is placed on a 10 cm square glass plate and covered with a slide glass put thereon. It is moved 10 times alternately 3 mm to the left and 3 mm to the right along the axis of the carbon fiber bundle and perpendicularly thereto. The change in yarn width that occurs during this operation is measured. The average of 10 measurements is adopted as an indicator of fiber spreading property. A larger degree of yarn width expansion indicates better fiber spreading property. Here, the fiber spreading property is evaluated according to the following criteria A to C depending on the ratio of the width of the opened carbon fiber bundle to that of the original sample.

A: The width after measurement is more than four times the original width.
B: The width after measurement is two times or more and less than four times the original width.
C: The width after measurement is less than two times the original width.

<Cross sectional shape of carbon fiber bundle>

[0067] The cross sectional shape of a carbon fiber bundle is measured as described below. The carbon fiber bundle is allowed to hang down by their own weight in a substantially untwisted and almost tension-free state, and the entire carbon fiber bundle is fixed by applying an adhesive or the like. After the adhesive has dried, the carbon fiber bundle is cut in such a manner that its cross section is not distorted. The exposed cross section of the carbon fiber bundle is observed using a polarizing microscope and its image is acquired. The acquired image is loaded into an open-source image analysis program (ImageJ (Version 1.53h)) and the contour of the filament cross section is traced using the "Polygon selections" tool. In doing this, 20 to 100 points selected on the contour are used to draw the whole contour of one cross section. Then, the traced contour is retouched into a smooth curve using the "Fit spline" tool. Then, the "Analyze particles" tool is used to obtain data on the size and position of the Feret diameter and the area inside the contour. Subsequently, the length of the line segment that intersects perpendicularly with the line segment of the Feret diameter and has the longest distance to the contour is determined. The cross sectional shape of the carbon fiber bundle is determined based on the area inside the contour, Feret diameter, and the length of the aforementioned line segment that intersects perpendicularly with the Feret diameter, and a calculation is made according to the following formula (2).

$$C / (A \times 2B) \qquad (2)$$

[0068] Here, A is the Feret diameter, B being the length of the aforementioned line segment that intersects perpendicularly with the Feret diameter, and C being the area inside the contour, which correspond to the letters shown in Figure 1. From the area of the rectangle defined by the two sides ($A \times 2B$) and the area inside the contour (C), the area ratio of the carbon fiber bundle cross section is calculated and the cross sectional shape is determined based thereon.

EXAMPLES

[Example 1]

[0069] A polyacrylonitrile based copolymer was polymerized by the solution polymerization method using dimethyl sulfoxide as solvent to prepare a spinning dope solution. A coagulated yarn was produced through a dry-wet spinning process in which the resulting spinning dope solution was first extruded into air through a spinneret and then introduced into a coagulation bath containing a 35 mass% aqueous solution of dimethyl sulfoxide maintained at 0°C.

[0070] This coagulated yarn was rinsed by an ordinary method and stretched 3.5 times in a double-tank warm water bath. Subsequently, this fiber bundle stretched in a water bath was treated with an amino-modified silicone based silicone oil solution and dried/densified using heated rollers at 160°C. It was stretched 3.7 times in pressurized steam so that the total stretching ratio of the yarn reached 13, and then it was subjected to entanglement treatment to provide a precursor fiber bundle containing 6,000 filaments. The precursor fiber bundle had a filament fineness of 0.7 dtex.

[0071] Next, the first flame resistant treatment step was set to a flame resistant treatment temperature of 250°C and a flame resistant treatment time of 11 minutes, and the second flame resistant treatment step was set to a flame resistant treatment temperature of 280°C and a flame resistant treatment time of 6 minutes (condition 1). Flame resistant treatment was performed under a tension of 0.8 mN/dtex in an oven with an air atmosphere. Two precursor fiber bundles were fed to each of the grooves on the rollers disposed before and after the flame resistant treatment furnace, thereby producing flame resistant treated fiber bundles. In addition, the precursor fiber bundles were twisted 15 turns per meter while they were subjected to flame resistant treatment.

[0072] The resulting flame resistant treated fiber bundles were subjected to preliminary carbonization treatment per-

formed at a stretching ratio of 1.20 in a nitrogen atmosphere at a maximum temperature of 800°C to provide preliminary carbonized fiber bundles. The resulting preliminary carbonized fiber bundles were subjected to carbonization treatment performed at a stretching ratio of 0.950 in a nitrogen atmosphere at a maximum temperature of 1 ,400°C. Here, in this carbonization step, the heating rate was 0.45°C/sec and the retention time at the maximum temperature was 60 seconds. The resulting carbon fiber bundles were subjected to surface treatment and coated with a sizing agent to provide final carbon fiber bundles, which had properties as shown in Tables 1 and 2.

[Example 2]

[0073] Except for performing flame resistant treatment under a tension of 1.0 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, twisting the carbon fiber precursor fiber bundles 15 turns per meter, and feeding three carbon fiber precursor fiber bundles to each of the grooves on the rollers disposed before and after the flame resistant treatment furnace, the same procedure as in Example 1 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 3]

[0074] Except for performing flame resistant treatment under a tension of 1.2 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, the same procedure as in Example 2 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 4]

[0075] Except for performing flame resistant treatment under a tension of 1.5 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, the same procedure as in Example 2 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 5]

[0076] Except for feeding two precursor fiber bundles to each of the grooves on the rollers disposed before and after the flame resistant treatment furnace, the same procedure as in Example 2 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 6]

[0077] Except for setting the first flame resistant treatment step to a flame resistant treatment temperature of 250°C and a flame resistant treatment time of 11 minutes while setting the second flame resistant treatment step to a flame resistant treatment temperature of 288°C and a flame resistant treatment time of 5 minutes (condition 2), performing the flame resistant treatment under a tension of 1.0 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, twisting the precursor fiber bundles 7 turns per meter, and feeding four precursor fiber bundles to each of the grooves on the rollers disposed before and after the flame resistant treatment furnace, the same procedure as in Example 1 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 7]

[0078] Except for setting the first flame resistant treatment step to a flame resistant treatment temperature of 250°C and a flame resistant treatment time of 11 minutes while setting the second flame resistant treatment step to a flame resistant treatment temperature of 283°C and a flame resistant treatment time of 5 minutes (condition 3), the same procedure as in Example 6 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 8]

[0079] Except for setting the first flame resistant treatment step to a flame resistant treatment temperature of 250°C and a flame resistant treatment time of 11 minutes while setting the second flame resistant treatment step to a flame resistant treatment temperature of 281°C and a flame resistant treatment time of 7 minutes (conditions 4), the same procedure as in Example 6 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles

obtained are described in Tables 1 and 2.

[Example 9]

[0080] Except for using precursor fiber bundles having a filament count of 8,000, the same procedure as in Example 8 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Example 10]

[0081] Except for using precursor fiber bundles having a filament fineness of 0.5 dtex and setting the first flame resistant treatment step to a flame resistant treatment temperature of 250°C and a flame resistant treatment time of 11 minutes while setting the second flame resistant treatment step to a flame resistant treatment temperature of 282°C and a flame resistant treatment time of 6 minutes (condition 5), the same procedure as in Example 8 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 1]

[0082] Except for performing flame resistant treatment under a tension of 0.6 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, and except that precursor fiber bundles were combined before twisting to have a filament count of 12,000, the same procedure as in Example 1 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 2]

[0083] Except for performing flame resistant treatment under a tension of 1.6 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step and performing flame resistant treatment at the temperatures according to the condition 2, the same procedure as in Comparative example 1 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 3]

[0084] Except for performing flame resistant treatment under a tension of 2.0 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step and performing flame resistant treatment at the temperatures according to the condition 6, the same procedure as in Comparative example 1 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 4]

[0085] Except for, as performed in Example 1 in Japanese Unexamined Patent Publication (Kokai) No. 2015-67910, setting the first flame resistant treatment step to a flame resistant treatment temperature of 240°C and a flame resistant treatment time of 30 minutes while setting the second flame resistant treatment step to a flame resistant treatment temperature of 280°C and a flame resistant treatment time of 30 minutes (condition 7), omitting the doubling of yarns before flame resistant treatment, and performing the carbonization treatment step under the conditions of a maximum temperature of 1,350°C, a stretching ratio of 0.960, a heating rate 1.50°C/sec in the carbonization step, and a retention time at the maximum temperature of 180 seconds, the same procedure as in Example 7 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 5]

[0086] Except for performing flame resistant treatment under a tension of 2.5 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, the same procedure as in Comparative example 4 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 6]

[0087] Except for performing flame resistant treatment under a tension of 1.5 mN/dtex, which was adjusted by changing

the stretching ratio in the flame resistant treatment step, the same procedure as Comparative example 4 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 7]

[0088] Except for performing flame resistant treatment under a tension of 0.6 mN/dtex, which was adjusted by changing the stretching ratio in the flame resistant treatment step, the same procedure as Comparative example 4 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Comparative example 8]

[0089] Except for performing the carbonization step at a heating rate of 0.90°C/sec, the same procedure as Comparative example 2 was carried out to produce carbon fiber bundles. Evaluation results of the carbon fiber bundles obtained are described in Tables 1 and 2.

[Table 1]

[0090]

Table 1

	flame resistant treatment condition					carbonization condition	carbon fiber										
							long diameter to short diameter ratio					strand characteristics			overall fineness	fiber spreading property	area ratio of cross section of carbon fiber bundle
	filament count	temperature condition	tension for flame resistant treatment	number of combined bundles	twisting angle	heatingrate in carbonization step	average value	coefficient of variation	skewness	proportion of filaments in the range of 1.00-1.03	proportion of filaments in the range of 1.04-1.10	elastic modulus	strength	elongation percentage			
unit	number		mN/dtex	number		°C/sec		%		%	%	GPa	GPa	%	g/m		
Example 1	6,000	1	0.8	2	1.9	0.45	1.04	2	0.8	40	40	302	6.1	2.0	0.27	B	0.69
Example 2	6,000	1	1.0	3	1.9	0.45	1.02	1	0.4	66	10	315	6.3	2.0	0.26	A	0.63
Example 3	6,000	1	1.2	3	1.9	0.45	1.03	2	1.0	50	20	317	6.2	1.9	0.25	B	0.67
Example 4	6,000	1	1.5	3	1.9	0.45	1.03	1	0.3	34	26	315	6.0	1.9	0.24	B	0.67
Example 5	6,000	1	1.0	2	1.9	0.45	1.03	2	1.1	40	20	288	6.4	2.2	0.27	B	0.70
Example 6	6,000	2	1.0	4	0.8	0.45	1.03	1	1.0	86	10	275	6.7	2.4	0.23	B	0.63
Example 7	6,000	3	1.0	4	0.8	0.45	1.02	1	1.1	84	10	278	6.8	2.4	0.23	B	0.64
Example 8	6,000	4	1.0	4	0.8	0.45	1.02	1	1.1	80	5	274	7.1	2.6	0.22	B	0.65
Example 9	8,000	4	1.0	4	0.8	0.45	1.02	1	1.2	76	12	276	6.9	2.5	0.29	A	0.62
Example 10	6,000	5	1.0	4	0.8	0.45	1.02	1	1.1	82	8	277	7.2	2.6	0.16	B	0.63
Comparative example 1	12,000	1	0.6	2	2.7	0.45	1.04	2	0.2	30	48	288	5.9	2.0	0.56	C	0.72
Comparative example 2	12,000	2	1.6	2	2.7	0.45	1.04	3	1.3	54	44	259	4.5	1.7	0.54	A	0.67

(continued)

	carbon fiber																									
	flame resistant treatment condition						carbonization condition	long diameter to short diameter ratio						strand characteristics			overall fineness	fiber spreading property	area ratio of cross section of carbon fiber bundle
	filament count	temperature condition	tension for flame resistant treatment	number of combined bundles	twisting angle		heating rate in carbonization step	average value	coefficient of variation	skewness	proportion of filaments in the range of 1.00-1.03	proportion of filaments in the range of 1.04-1.10	elastic modulus	strength	elongation percentage			
Comparative example 3	12,000	6	2.0	2	2.7		0.45	1.06	5	1.7	44	54	276	5.5	2.0	0.56	B	0.71
Comparative example 4	6,000	7	1.0	1	0.8		1.50	1.04	2	0.2	32	52	325	5.6	1.7	0.32	C	0.75
Comparative example 5	6,000	7	2.5	1	0.8		1.50	1.04	2	0.2	28	46	290	5.5	1.9	0.29	C	0.73
Comparative example 6	6,000	7	1.5	1	0.8		1.50	1.04	2	0.2	30	50	323	5.2	1.6	0.30	C	0.73
Comparative example 7	6,000	7	0.6	1	0.8		1.50	1.04	2	0.2	34	56	323	5.3	1.6	0.33	C	0.76
Comparative example 8	12,000	2	1.6	2	2.7		0.90	1.04	3	1.3	54	44	245	4.2	1.7	0.54	A	0.68

[Table 2]

[0091]

Table 2

	after first flame resistant treatment	after second flame resistant treatment	
	1,453/1,370 cm^{-1}	1,453/1,370 cm^{-1}	1,254/1,370 cm^{-1}
Condition 1	1.01	0.73	0.63
Condition 2	1.01	0.70	0.60
Condition 3	1.01	0.71	0.62
Condition 4	1.01	0.71	0.61
Condition 5	1.01	0.71	0.61
Condition 6	1.01	0.70	0.60
Condition 7	0.90	0.56	0.56

Explanation of numerals

[0092]

A Feret diameter
B length of line segment that intersects perpendicularly with Feret diameter
C area inside the contour

INDUSTRIAL APPLICABILITY

[0093] The carbon fiber bundle according to the present invention is a carbon fiber suitable for fabric reinforcing material production that shows a good balance between excellent mechanical properties inherent in carbon fibers and a desirable flattened cross section of the carbon fiber bundle. The use of the carbon fiber bundle according to the present invention allows a high-performance fabric reinforcing material to be produced with high productivity.

Claims

1. A carbon fiber bundle comprising a plurality of filaments **characterized by** having a strand elastic modulus of 260 to 350 GPa, a strand strength of 6.0 to 8.5 GPa, an elongation percentage of 1.8% or more, a filament count of 1,000 to 9,000, an overall fineness of 0.15 to 0.35 g/m, wherein the filament cross sections have an average long diameter to short diameter ratio of 1.01 to 1.08, a coefficient of variation of 1% to 4%, and a skewness of 0.3 to 1.2.

2. A carbon fiber bundle as set forth in claim 1, wherein the cross section of the carbon fiber bundle has an area ratio 0.50 to 0.70.

3. A carbon fiber bundle as set forth in either claim 1 or 2, wherein the elongation percentage is 2.0% or more.

4. A carbon fiber bundle as set forth in any one of claims 1 to 3, wherein the elongation percentage is 2.2% or more.

5. A carbon fiber bundle as set forth in any one of claims 1 to 4, wherein the proportion of filaments with long diameter to short diameter ratios of 1.04 to 1.10 is in the range of 10% to 40%.

6. A carbon fiber bundle as set forth in any one of claims 1 to 5, wherein the proportion of filaments with long diameter to short diameter ratios of 1.00 to 1.03 is in the range of 30% to 90%.

7. A production method for carbon fiber bundles, comprising:

a first flame resistant treatment step for subjecting polyacrylonitrile based carbon fiber precursor fiber bundles to flame resistant treatment performed for 8 to 25 minutes until the ratio of the peak intensity at 1,453 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum comes into the range of 0.98 to 1.10,
a second flame resistant treatment step for performing additional flame resistant treatment performed for 5 to 20 minutes until the ratio of the peak intensity at 1,453 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum comes into the range of 0.70 to 0.75 while at the same time the ratio of the peak intensity at 1,254 cm^{-1} to the peak intensity at 1,370 cm^{-1} in the infrared spectrum comes into the range of 0.50 to 0.65, wherein the twist angle of the fiber bundles is maintained at 0.2° or more during the flame resistant treatment while maintaining the tension on the fiber bundles at 0.7 to 1.5 mN/dtex during the flame resistant treatment, and feeding a plurality of fiber bundles to each of the grooves on the rollers,
a preliminary carbonization step for subjecting the fiber bundles resulting from the first and second flame resistant treatment steps to preliminary carbonization performed in an inactive atmosphere at a maximum temperature of 500°C to 1,200°C and a stretching ratio of 1.00 to 1.20.,
a carbonization step for subjecting the fiber bundles resulting from the preliminary carbonization step to carbonization performed in an inactive atmosphere at a maximum temperature of 1,000°C to 1,500°C, and
a step for subjecting the fiber bundles resulting from the carbonization step to electrolytic surface treatment to produce carbon fiber bundles.

8. A production method for carbon fiber bundles as set forth in claim 7, wherein in the carbonization step, treatment at the maximum temperature is continued for 20 to 60 seconds and the heating rate is 0.40°C/sec to 1.10°C/sec.

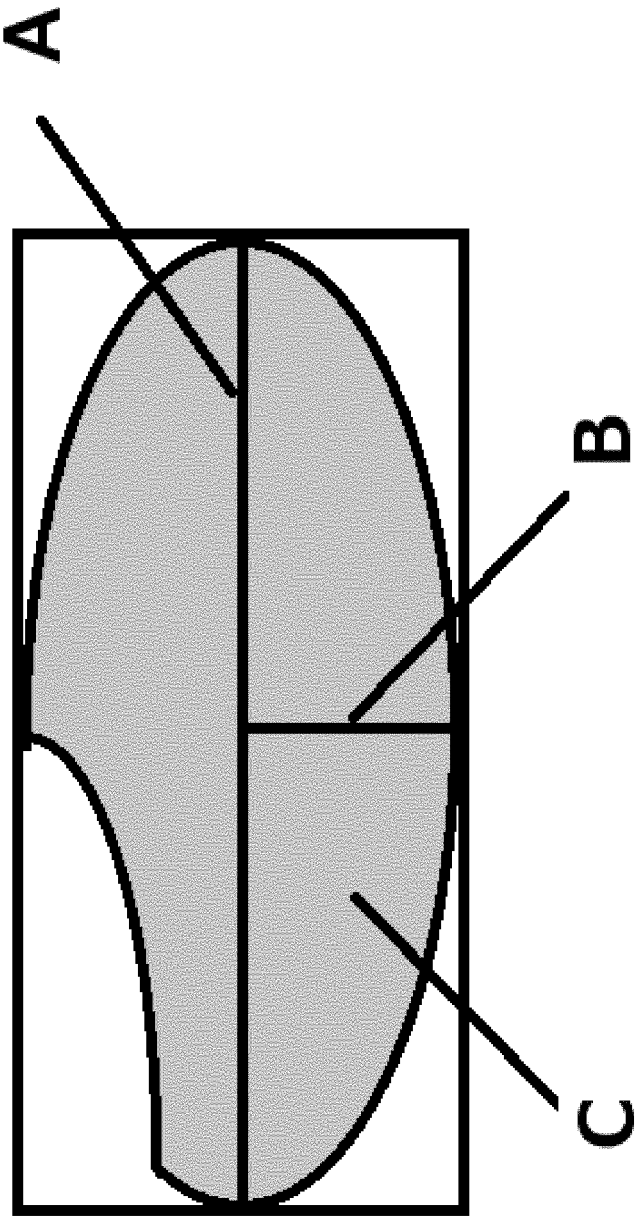

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/031179

A. CLASSIFICATION OF SUBJECT MATTER

D01F 9/22(2006.01)i; ***D01F 6/18***(2006.01)i
FI: D01F9/22; D01F6/18 E

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)

D01D9/22; 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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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.
Y	JP 2021-59829 A (TORAY INDUSTRIES, INC.) 15 April 2021 (2021-04-15) claims 1, 11, paragraph [0046], examples	7-8
A		1-6
Y	JP 2017-128838 A (TORAY INDUSTRIES, INC.) 27 July 2017 (2017-07-27) claims 1, 8, paragraph [0056]	7-8
A		1-6
A	WO 2021/090641 A1 (TORAY INDUSTRIES, INC.) 14 May 2021 (2021-05-14)	1-8
A	JP 2002-294518 A (MITSUBISHI RAYON CO LTD) 09 October 2002 (2002-10-09)	1-8
A	JP 2002-69754 A (TOHO TENAX CO LTD) 08 March 2002 (2002-03-08)	1-8
A	JP 11-269727 A (TORAY INDUSTRIES, INC.) 05 October 1999 (1999-10-05)	1-8

☐ 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	Date of mailing of the international search report
11 October 2022	**25 October 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/031179

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2021-59829 A	15 April 2021	(Family: none)	
JP 2017-128838 A	27 July 2017	(Family: none)	
WO 2021/090641 A1	14 May 2021	(Family: none)	
JP 2002-294518 A	09 October 2002	(Family: none)	
JP 2002-69754 A	08 March 2002	(Family: none)	
JP 11-269727 A	05 October 1999	(Family: none)	

Form PCT/ISA/210 (patent family annex) (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

- JP SHO58191244 A **[0007]**
- JP 2017137614 A **[0007]**
- WO 201668034 A **[0007]**
- JP 2015067910 A **[0007] [0085]**
- JP 2021059829 A **[0007]**