

## DESCRIPTION

### TITLE OF THE INVENTION

CARBON-FIBER CHOPPED STRAND AND MANUFACTURING METHOD  
OF THE SAME

### TECHNICAL FIELD

[0001]

The present invention relates to a carbon-fiber chopped  
strand which is an important raw material for production of  
short-carbon-fiber-reinforced thermoplastic resin, as well as  
to a manufacturing method of the carbon-fiber chopped strand.  
More particularly, the present invention relates to a carbon-  
fiber chopped strand of high flowability and a manufacturing  
method thereof. The carbon-fiber chopped strand of the  
present invention can be fed smoothly from the hopper of  
extruder into a meter, in production of, for example, carbon  
fiber-containing resin pellets or carbon fiber-containing  
resin shaped article.

### BACKGROUND ART

[0002]

Short-carbon-fiber-reinforced thermoplastic resin  
(hereinafter referred to as "CFRTP") produced using a  
thermoplastic resin as a matrix resin, has drawn attention as  
a high-performance engineering material, and the demand  
therefor is increasing rapidly. This CFRTP can be produced  
by injection molding and accordingly is high in productivity.  
Moreover, the CFRTP, as compared with conventional non-  
reinforced thermoplastic resins or short-glass-fiber-

reinforced thermoplastic resins, is superior in mechanical properties, sliding property, electrical properties, dimensional stability, etc.

As the method for producing the CF RTP, there are  
5 ordinarily the following methods.

[0003]

(1) First, there is fed, into an extruder, a carbon-fiber filament bundle cut into 3 to 10 mm and bundled with a sizing agent (a so-called carbon-fiber chopped strand)  
10 or a so-called milled carbon fiber ground into 1 mm or shorter, together with pellets or a powder of thermoplastic resin; and they are melt-kneaded therein to obtain pellets. Then, the pellets are made into a CF RTP using an injection molding machine or an extrusion  
15 molding machine.

[0004]

(2) A carbon-fiber chopped strand is fed into an extrusion molding machine together with pellets or a powder of thermoplastic resin to directly produce a CF RTP.

20 [0005]

Meanwhile, as the method for feeding a carbon-fiber chopped strand and a thermoplastic resin into an extruder to produce pellets, the following methods are employed mainly.

(1) A method of dry-blending a carbon-fiber chopped strand  
25 and a thermoplastic resin and feeding the resulting blend into an extruder (a dry-blending method).

(2) A method of feeding a thermoplastic resin into the rear end side (in extrusion direction) of extruder and feeding a carbon-fiber chopped strand to the  
30 intermediate portion (in extrusion direction) of

extruder wherein the fed thermoplastic resin is in a molten state (a side-feeding method).

[0006]

As well known, the properties of CF RTP are related to the fiber length of the carbon fiber of CF RTP. When there is used a milled fiber of extremely short fiber length, the fiber length in the molded CF RTP is extremely short; accordingly, the properties of this CF RTP are inferior to those of CF RTP using a carbon-fiber chopped strand.

10 [0007]

In order to keep long the fiber length of CF RTP, there is a case that a CF RTP is produced using a long fiber pellet having a fiber length same as the cut length of carbon-fiber chopped strand. In this case, the fiber direction in the CF RTP obtained is difficult to control. Therefore, this method of CF RTP production using a long fiber pellet is disadvantageous for production of an inexpensive CF RTP which needs to be mass-produced. For the above reasons, carbon-fiber chopped strand is generally used in production of CF RTP.

20 [0008]

In production of CF RTP, when the carbon-fiber chopped strand used is low in flowability, there is a problem that stable feeding of carbon-fiber chopped strand into extruder is difficult.

25 [0009]

In the dry-blending, when the carbon-fiber chopped strand used is low in flowability, there is a problem that the carbon-fiber chopped strand is difficult to flow down in the hopper of extruder or injection molding machine. As a result, the feeding of the carbon-fiber chopped strand in a

give amount from the meter provided at the bottom of hopper,  
to the extrusion screw of extruder becomes unstable. For the  
above reason, it is difficult to obtain a CF RTP of uniform  
composition stably and, moreover, the production efficiency  
5 is low.

[0010]

Meanwhile, in the side-feeding method as well, when the  
carbon-fiber chopped strand used is low in flowability, the  
carbon-fiber chopped strand is not fed stably into the  
10 extrusion screw of extruder and, in an extreme case, the  
feeding itself of the carbon-fiber chopped strand may be  
impossible.

[0011]

For these reasons, a carbon-fiber chopped strand used  
15 industrially in a large amount is required to have high  
flowability. In order to respond to this requirement, it is  
conducted to add a sizing agent of high bundling ability to a  
carbon-fiber chopped strand or add a sizing agent in a large  
amount. It is also conducted to add another sizing agent to  
20 a carbon-fiber chopped strand obtained by cutting a strand,  
to mold the carbon-fiber chopped strand into a rice grain  
shape.

[0012]

However, in producing a CF RTP by mixing the above-  
25 mentioned chopped strand containing a large amount of a  
sizing agent, with a heat-resistant thermoplastic resin of  
high processing temperature, a gas is generated by the  
thermal decomposition of the sizing agent. This gas allows  
the obtained CF RTP to have poor appearance or low weld  
30 strength (see, for example, Patent Literatures 1 and 2).

Further, the thermal decomposition of the sizing agent tends to cause reduction in properties of CFRTP.

[0013]

Further, in melt-kneading a chopped strand with a thermoplastic resin in an extruder, there is a case that the sizing agent added in a large amount to the carbon fiber of chopped strand reduces the dispersibility of the carbon fiber. In this case, the dispersibility of carbon fiber in the pellet obtained is insufficient. When a CFRTP is produced using this pellet, there are present, in the CFRTP produced, fiber bundles not dispersed sufficiently. The fiber bundles become a center of stress concentration, reducing the mechanical properties (particularly, tensile strength) of the CFRTP.

[0014]

Meanwhile, in order to produce a chopped strand in a large amount, it is effective to increase the number of single filaments constituting the chopped strand. Chopped strands composed of 30,000 or more single filaments are known. Such a chopped strand has a flat shape. The flat shape makes easy the single-filament-state dispersion of carbon fiber in CFRTP, whereby the assembling of carbon fibers in bundle shape can be avoided.

[0015]

However, the chopped strand of flat shape has a large surface area, resulting in a large contact area between chopped strands. Consequently, the chopped strand has low flowability and, in feeding the chopped strand into an extruder, there arises poor feeding into meter or extruder.

[0016]

Further, the above poor feeding makes long the residence time of chopped strand in extruder. In this case, the chopped strand undergoes larger shear by the screw of extruder and the breakage of carbon fiber takes place. As a result, the fiber length becomes short, resulting in reduction in mechanical properties of the CFRTP obtained.  
[0017]

As described above, it has been difficult to allow a carbon-fiber chopped strand to have high flowability without reducing the dispersibility of carbon fiber and the properties of the CFRTP obtained and thereby to feed the chopped strand in a large amount in a stable state from the hopper of extruder to the extrusion screw of extruder.

Patent Literature 1: JP-A-2003-165849

15 Patent Literature 2: JP-A-2004-149725

## DISCLOSURE OF THE INVENTION

### Task to Be Achieved by the Invention

[0018]

20 The present inventor made a study in order to solve the above problems. As a result, it was found that a chopped strand obtained by adding twists of 0.5 to 50 times per meter to a carbon-fiber strand in which 30,000 or more single filaments are bundled, then adding a 1 to 10 mass % of a sizing agent to the twisted strand to bundle the single filaments, thereafter cutting the resulting strand into a given shape is highly dispersed in the CFRTP produced with the strand, unexpectedly. It was further found that this chopped strand is not flat, accordingly has high flowability, and flows down smoothly in a hopper.

[0019]

The above findings have led to the completion of the present invention. Therefore, the present invention aims at providing a carbon-fiber chopped strand which allows large-size packing suitable for mass production, which can be fed stably into an extruder from a hopper, and which shows good dispersibility of carbon fiber in the kneading operation in extruder, and a manufacturing method of such a carbon-fiber chopped strand.

#### 10 **Means for Achieving the Task**

[0020]

The above aim of the present invention can be achieved by following various inventions of the present invention.

[0021]

- 15 [1] A carbon-fiber chopped strand composed of 30,000 to 120,000 carbon fiber single filaments and 1 to 10 mass % of a sizing agent which bundles the single filaments, in which carbon-fiber chopped strand the ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both  
20 of the section of chopped strand is 1.0 to 1.8, the length ( $L$ ) of chopped strand along the fiber direction is 3 to 10 mm, and the repose angle of chopped strand is 10 to 30°.

[0022]

- [2] The carbon-fiber chopped strand according to [1],  
25 wherein the ratio ( $L/D_{\min}$ ) of the length ( $L$ ) of chopped strand along the fiber direction and the minimum diameter ( $D_{\min}$ ) of chopped strand is 4 or smaller.

[0023]

- [3] The carbon-fiber chopped strand according to [1],  
30 wherein the sizing agent is a polyamide resin.

[0024]

[4] A method for manufacturing a carbon-fiber chopped strand set forth in [1], characterized by comprising

5 a step of twisting, by 0.5 to 50 times per meter, an untwisted carbon-fiber strand composed of 30,000 to 120,000 single filaments,

a step of introducing the twisted carbon-fiber strand into a sizing agent bath, followed by drying, to adhere 1 to 10 mass % of the sizing agent to the twisted carbon-fiber strand to allow a carbon-fiber strand bundled, and

10 a step of cutting the carbon-fiber strand bundled into a given length.

[0025]

[5] The method for manufacturing a carbon-fiber chopped strand, set forth in [4], wherein the sizing agent is a polyamide resin and the sizing agent concentration in sizing agent bath is 0.5 to 30 mass %.

[0026]

[6] An assembly of carbon-fiber chopped strands each  
20 composed of 30,000 to 120,000 carbon fiber single filaments and 1 to 10 mass % of a sizing agent which bundles the single filaments, in each carbon-fiber chopped strand the ratio ( $D_{max}/D_{min}$ ) of the maximum diameter ( $D_{max}$ ) and the minimum diameter ( $D_{min}$ ) both of the section of chopped strand being  
25 1.0 to 1.8, the length (L) of chopped strand along the fiber direction being 3 to 10 mm, and the repose angle of chopped strand being 10 to 30°, in which assembly the remaining ratio of original carbon-fiber chopped strands bundled is 70% or higher.

30 [0027]

[7] A package of carbon-fiber chopped strands, comprising carbon-fiber chopped strands each composed of 30,000 to 120,000 carbon fiber single filaments and 1 to 10 mass % of a sizing agent which bundles the single filaments, in each carbon-fiber chopped strand the ratio ( $D_{max}/D_{min}$ ) of the maximum diameter ( $D_{max}$ ) and the minimum diameter ( $D_{min}$ ) both of the section of chopped strand being 1.0 to 1.8, the length (L) of chopped strand along the fiber direction being 3 to 10 mm, and the repose angle of chopped strand being 10 to 30°, and

a flexible container bag which packs the carbon-fiber chopped strands, in which package the remaining ratio of original carbon-fiber chopped strands bundled is 70% or higher.

[0028]

[8] A method for manufacturing pellets each composed of a thermoplastic resin and a carbon fiber dispersed in the thermoplastic resin, using an extruder, which method comprising

a step of feeding directly into the hopper of an extruder from a flexible container bag, carbon-fiber chopped strands each composed of 30,000 to 120,000 carbon fiber single filaments and 1 to 10 mass % of a sizing agent which bundles the single filaments, in which carbon-fiber chopped strands the ratio ( $D_{max}/D_{min}$ ) of the maximum diameter ( $D_{max}$ ) and the minimum diameter ( $D_{min}$ ) both of the section of chopped strand is 1.0 to 1.8, the length (L) of chopped strand along the fiber direction is 3 to 10 mm, and the repose angle of chopped strand is 10 to 30°, and

a step of kneading, in the extruder, the carbon-fiber

chopped strands with a resin.

#### **Effect of the Invention**

[0029]

In the carbon-fiber chopped strand of the present  
5 invention, there is used, as the raw material, a carbon-fiber  
strand obtained by impregnating a given amount of a sizing  
agent into a carbon-fiber strand composed of 30,000 to  
120,000 single filaments. Since this carbon-fiber strand has  
a twist of 0.5 to 50 times per meter, the carbon-fiber  
10 chopped strand of the present invention obtained by cutting  
the strand is superior in bundling ability and hardly has a  
flat sectional shape. Consequently, the present carbon-fiber  
chopped strand is superior in flowability.

[0030]

15 Accordingly, when the present carbon-fiber chopped  
strand is fed into the hopper of extruder, the strand flows  
down smoothly in the hopper and the strand is fed stably into  
the meter of extruder. As a result, the chopped strand can  
be fed stably to the extrusion screw of extruder.

20 [0031]

The present carbon-fiber chopped strand can be fed  
stably into an extruder, as mentioned above; therefore, there  
is hardly fluctuation in the time in which the strand passes  
through the extruder, enabling the shortening of the  
25 residence time of chopped strand in extrusion screw. As a  
result, there is little cutting of strand in kneading in  
extrusion screw, whereby is obtained a molding material in  
which a long fiber is dispersed. For this reason, there can  
be obtained, by using the molding material, a molded article  
30 of excellent mechanical properties.

## BEST MODE FOR CARRYING OUT THE INVENTION

[0032]

The carbon-fiber chopped strand of the present  
5 invention is produced by the following method.

[0033]

The carbon fiber used as a raw material in production  
of the present carbon-fiber chopped strand is a filament-like  
carbon fiber which can be twisted.

10 As the carbon fiber, there can be used, for example, a  
carbon fiber of polyacrylonitrile (PAN) type, rayon type,  
pitch type or the like (including a graphite fiber) and a  
carbon fiber obtained by coating a metal on the surface of  
the former carbon fiber.

15 The single-filament diameter of the carbon fiber is  
preferably 3 to 15  $\mu\text{m}$ , more preferably 5 to 10  $\mu\text{m}$ .

[0034]

The carbon fiber is produced by a known method and is  
ordinarily supplied in the form of strand. The number of the  
20 single filaments constituting the strand is preferably 30,000  
to 120,000, more preferably 40,000 to 110,000, particularly  
preferably 50,000 to 100,000.

[0035]

In the current manufacturing method of the carbon fiber,  
25 the production cost depends upon the number of the single  
filaments constituting a strand and the diameter of single  
filament. Accordingly, a strand composed of single filaments  
of less than 30,000 is usable but is high in production cost.  
Moreover, such a strand is not economical as a reinforcing  
30 material for CFRTP which needs to be low in cost.

[0036]

A strand composed of single filaments of more than 120,000 is difficult to impregnate a sizing agent thereinto, in adhering the sizing agent to the strand. Therefore, in  
5 the sizing agent-adhered strand, the bundling ability tends to be low. Such a strand tends to be split along the fiber axis direction of strand, in cutting of strand into chopped strand. Further, it is not preferable, because the strand tends to be low in uniform dispersibility of carbon fibers in  
10 the pellets or CF RTP produced by melt-kneading of chopped strand with resin.

[0037]

The mass per unit length, of single filament is appropriately 0.8 to 8.0 g/m.

15 [0038]

The above-mentioned carbon-fiber strand is then twisted 0.5 to 50 times per meter. When the twist is less than 0.5 times per meter, the chopped strand obtained has a flat sectional shape. That is, there is obtained a carbon-fiber  
20 chopped strand of flat shape, having a ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both of the section of chopped strand, of larger than 1.8. As a result, the chopped strand has low flowability.

[0039]

25 When the twist is more than 50 times per meter, the sizing agent hardly impregnates into the inner portion of fiber bundle. As a result, when the fiber strand is cut, the carbon fibers of the inner portion of strand, not impregnated with the sizing agent are released outside and form a mass of  
30 cotton-fiber-like fluff, resulting in a chopped strand of low

flowability.

[0040]

The carbon-fiber strand twisted 0.5 to 50 times per meter may be produced also by a method of twisting a precursor (a carbon fiber precursor) such as oxidized fiber bundle or the like and then carbonizing the twisted precursor according to an ordinary means.

[0041]

It is ordinarily preferred that the twist is applied after the carbonization of the precursor. When the twist is applied to a carbon fiber strand after carbonization, a sizing agent may be adhered to a non-twisted carbon fiber strand and then twist may be applied. Or, twist may be applied before adhesion of sizing agent and then a sizing agent may be adhered. It is generally preferred that twist is applied and then a sizing agent is adhered.

[0042]

The sizing agent used in the present invention is preferably various thermoplastic resins and thermosetting resins. There can be mentioned, for example, epoxy resin, urethane-modified epoxy resin, polyester resin, phenolic resin, polyamide resin, polyurethane resin, polycarbonate resin, polyetherimide resin, polyamideimide resin, polystyrypyridine resin, polyimide resin, bismaleimide resin, polysulfone resin, polyethersulfone resin, epoxy-modified urethane resin, polyvinyl alcohol resin, polyvinylpyrrolidone resin, and modified resins thereof. Mixtures thereof are also used. Of them, epoxy resin, urethane-modified epoxy resin, polyurethane resin and polyamide resin are preferred, and polyamide resin is particularly preferred for the wide

usability, easy handling and high function. As the polyamide resin, 8 Nylon (trade mark) which is a soluble nylon resin, is particularly preferred.

[0043]

5           The amount of the sizing agent adhered to the carbon-fiber strand is 1 to 10 mass %, preferably 3 to 8 mass %, more preferably 4 to 7 mass %, based on the total mass of carbon fiber strand and sizing agent.

[0044]

10           When the amount of sizing agent is less than 1 mass %, the carbon-fiber chopped strand obtained has low bundling ability and tends to split during the transportation and handling.

[0045]

15           When the amount of sizing agent is more than 10 mass %, the dispersibility of carbon fibers is low in kneading of carbon-fiber strand with molten resin to produce pellets or CF RTP. As a result, the pellets or the like obtained is low in mechanical properties. Further, the amount of the thermal  
20 decomposition gas generated in kneading is large, deteriorating the CF RTP produced. Furthermore, cutting of strand is difficult, tending to produce a chopped strand having a flat sectional shape. Therefore, the section of chopped strand hardly becomes a shape close to a circle,  
25 resulting in low flowability.

[0046]

          The sizing agent is adhered to the carbon-fiber strand ordinarily in the form of a solution dissolved in a solvent or a dispersion dispersed in a solvent. As the solvent,  
30 there is selected from water, an alcohol (e.g. ethyl alcohol

or methyl alcohol), a ketone (e.g. acetone or methyl ethyl ketone), an aromatic solvent (e.g. toluene or xylene), dichloromethane, N-methylpyrrolidone, dimethylformamide, tetrahydrofuran, etc., depending upon the kind of the sizing agent used. An appropriate mixture thereof may also be selected. The concentration of sizing agent in sizing agent solution or sizing agent dispersion is preferably 0.5 to 30 mass %.

[0047]

In order to adhere the sizing agent to the carbon-fiber strand, there is employed a known method, for example, a method of dipping a carbon-fiber strand in a sizing agent solution or a method of spraying a sizing agent solution using a spray nozzle.

[0048]

The sizing agent-adhered carbon-fiber strand is then dried by a known method. The drying is conducted, for example, by passing the strand through an air dryer or the like. The drying temperature is preferably 50 to 200°C. By such drying, the section of carbon-fiber strand intersecting at right angles with the fiber axis direction becomes nearly circular spontaneously owing to the twisting and the bundling action of sizing agent, and the ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both of the section comes to fall in a range of 1.0 to 1.8.

[0049]

Incidentally, in the above drying, the shaping of the section of the sizing agent-adhered carbon-fiber strand may be conducted using a grooved roller. The sectional shape of the groove of roller is preferably a U shape.

[0050]

The carbon-fiber strand bundled produced as above is then cut into 3 to 10 mm, preferably 5 to 8 mm, whereby the carbon-fiber chopped strand of the present invention is  
5 obtained. The average diameter of the present carbon-fiber chopped strand differs depending upon the number of bundled single filaments but is ordinarily 1 to 10 mm.

[0051]

In the present carbon-fiber chopped strand, the ratio  
10 ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) in a section intersecting at right angles with the fiber axis direction is 1.0 to 1.8, preferably 1.0 to 1.6. A ratio exceeding 1.8 is not preferred because the contact area between strands is large and the flowability of  
15 strand is low.

[0052]

In the present chopped strand, the fiber length ( $L$ ) is preferably 3 to 10 mm, more preferably 5 to 8 mm. A fiber length of chopped strand exceeding 10 mm is not preferred  
20 because the contact area between strands is large and the flowability of strand is low. Meanwhile, a fiber length of chopped strand of shorter than 3 mm is not preferred because no sufficient reinforcing effect is obtained when a fiber-reinforced composite material has been produced.

25 [0053]

The ratio ( $L/D_{\min}$ ) of the fiber length ( $L$ ) of chopped strand and the minimum diameter ( $D_{\min}$ ) of chopped strand is preferably 4 or smaller, more preferably 3 or smaller. With a ratio of larger than 4, the contact area between strands is  
30 large and the flowability of strand may be low.

[0054]

The flowability of carbon-fiber chopped strand is evaluated by its repose angle. The repose angle is measured by a method described later. A smaller repose angle is  
5 interpreted to indicate a higher flowability. The repose angle of a chopped strand interpreted to have good flowability is preferably  $30^{\circ}$  or smaller, more preferably  $25^{\circ}$  or smaller. A repose angle exceeding  $30^{\circ}$  is not preferred because the chopped strand does not flow down stably in  
10 feeding of chopped strand in hopper, into extruder. A repose angle of smaller than  $10^{\circ}$  is not preferred because the chopped strand has too high flowability, making difficult the handling thereof.

[0055]

15 The bulk density of carbon-fiber chopped strand is indicated by the mass of chopped strand per given volume (1 L). The bulk density of the present carbon-fiber chopped strand is preferably 200 g/L or higher, more preferably 250 g/L, particularly preferably 300 g/L or higher. The upper  
20 limit of the bulk density is ordinarily 700 g/L.

[0056]

In general, when the bulk density is 150 g/L or lower, the frictional resistance at the interface between chopped strands is larger than the gravity which each chopped strand  
25 receives. As a result, there appear, in the hopper, those chopped strands unable to flow down partly.

[0057]

The stability of shape retainability of chopped strand can be examined by measuring the ratio of generation of free  
30 fiber. The ratio of generation of free fiber is desirably 3%

or lower. When the ratio of generation of free fiber is 5% or higher, the shape of chopped strand is not retainable during the transportation of chopped strand or in feeding of chopped strand from hopper into extruder, and the opening of  
5 chopped strand takes place. As a result, cotton-like masses are formed, reducing the flowability of chopped strand.

The ratio of generation of free fiber was measured by the following method.

[0058]

10 A carbon-fiber chopped strand was dropped into a 500-ml beaker from a height of 30 cm above the beaker. The carbon-fiber chopped strand was fed until the strand piled up in the beaker so as to exceed the upper end of the beaker and  
15 dropped from the upper end of the beaker. Then, a glass rod was moved along the upper end of the beaker to remove the portion of carbon-fiber chopped strand projecting upward from the upper end surface of the beaker. Then, the mass (W1 g) of the carbon-fiber chopped strand in the beaker was measured.

[0059]

20 Then, the carbon-fiber chopped strand was transferred into a 2,000-ml graduated cylinder, and the cylinder was sealed tightly. The graduated cylinder was rotated at 25 rpm for 20 minutes on the axis of graduated cylinder. The  
25 rotation of graduated cylinder was stopped and the carbon-fiber chopped strand was transferred onto a sieve (3 meshes). The sieve was moved in all directions until there was no dropping of carbon-fiber chopped strand from the eyes of sieve, for sifting of carbon-fiber chopped strand. The free  
30 fiber remaining on the sieve was collected and its mass (W2 g) was measured. The ratio of generation of free fiber was

calculated using the following formula.

$$\text{Ratio of generation of free fiber (\%)} = (W2/W1) \times 100$$

The chopped strand of the present invention is packed in a flexible container bag or the like, in a state of assembly of a large number of chopped strands, and is supplied to a pellet production step. In this case, it is preferred that the chopped strands of assembly form or package form do not split into chopped strands of smaller number of single filaments and stably keep the chopped strands of original number of single filaments.

[0060]

The degree of splitting of strands is indicated by the remaining ratio of original carbon-fiber chopped strands which is described later. The remaining ratio of original carbon-fiber chopped strands is preferably 50% or higher, more preferably 70% or higher. A remaining ratio of original carbon-fiber chopped strands, of lower than 50% is not preferred because the contact area between strands is large and the flowability of chopped strand is low.

[0061]

The packing of chopped strands can be conducted using a known method. A method of using a flexible container bag is preferably used. The flexible container bag is a bag-shaped packing material which is used for storage or transportation of powdery substance or granular substance. As the flexible container bag, a commercial product can be used appropriately. The flexible container bag is preferably a type which can be opened at the bottom. The flexible container bag makes easy the feeding operation of chopped strands into hopper.

By employing the above operation, the carbon-fiber

chopped strand of the present invention can be obtained.

#### EXAMPLES

[0062]

5           The present invention is described more specifically below by way of Examples. However, the present invention is in no way restricted by these Examples.

[0063]

(Decomposition method by sulfuric acid)

10           The quantitative determination of sizing agent was conducted by so-called decomposition method by sulfuric acid which is described below.

          2 g (W1) of a carbon-fiber chopped strand was placed in a 200-ml conical beaker and weighed accurately. 100 ml of  
15 concentrated sulfuric acid was added and the beaker was covered with a watch glass. The beaker was heated at about 200°C for 1 hour to thermally decompose the sizing agent of the chopped strand. After cooling, an aqueous hydrogen peroxide solution was added into the beaker in small portions  
20 until the solution in the beaker became transparent. Then, the carbon fiber in the beaker was separated by filtration, using an accurately weighed glass filter (W2). The separated carbon fiber was washed with about 1,000 ml of water and then the glass filter containing the carbon fiber was dried at  
25 110±3°C for 2 hours. The mass (W3) of the glass filter containing the carbon fiber, after drying was weighed accurately.

[0064]

          The amount of the sizing agent adhered was determined  
30 by the following formula.

Amount of sizing agent adhered (mass %) =

$$(W1 - (W3 - W2)) \times 100 / W1$$

(Remaining ratio of original chopped strands)

1 g of chopped strands was weighed. There were

5 measured the total number of the weighed chopped strands and  
the number of original chopped strands each retaining the  
original number of single filaments. Using these measurement  
data, the remaining ratio of original chopped strands each  
retaining the original number of single filaments was  
10 calculated.

[0065]

(Bulk density)

300 g of chopped strands was filled in a 2-L graduated

cylinder. Slight impact was applied continuously. A volume

15 of the chopped strands was measured when there was no change  
in the volume of the chopped strands filled. Using this  
volume and the mass of the chopped strands, the bulk density  
of the chopped strands was calculated.

[0066]

20 (Measurement method of repose angle)

40 g of carbon-fiber chopped strands was filled in a

funnel having a lower diameter of 18 mm, and was allowed to

fall freely onto a floor surface from a height of 100 mm.

There were measured the height (h) of the chopped strands

25 accumulated on the floor surface and a half of the diameter

(r) of floor area on which the chopped strands piled up. The

angle (repose angle,  $\theta$ ) formed by the floor surface and the

slope of chopped strand mountain was calculated using the  
following formula.

30 
$$\tan \theta = h/r$$

[0067]

Examples 1 to 6 and Comparative Examples 1 to 4

A non-twisted, PAN-based carbon-fiber strand (Tenax STS 40-48K, a product of Toho Tenax Co., Ltd.) composed of 48,000  
5 single filaments was twisted continuously to obtain carbon-fiber strands each having a twist described in Table 1. Each twisted carbon-fiber strand was introduced continuously into a sizing agent bath at a speed of 4 m/min to impregnate the strand with the sizing agent. The sizing agent was a  
10 methanol solution of soluble 8 Nylon Resin (LUCKAMIDE 5003, a product of DIC Co., Ltd.). In this case, the concentration of sizing agent solution was adjusted to control the sizing agent amount in carbon-fiber strand, at a level shown in Table 1. By this operation, each carbon-fiber strand  
15 received a bundling treatment.

[0068]

The resulting carbon-fiber strand was passed through a grooved roller (the groove had a rectangular sectional shape of 3 mm in width and 2 mm in depth). Then, each carbon-fiber  
20 strand was sent to an air drier (140°C) to dry the strand. The strand came to have a roughly circular section by being passed through the grooved roller. Then, each dried carbon-fiber strand was cut into a length of 6 mm to obtain carbon-fiber chopped strands. The carbon-fiber chopped strands were  
25 measured for repose angle and bulk density by the above-mentioned methods. Next, 200 kg of the carbon-fiber chopped strands was packed in a flexible container bag which was openable at the bottom. Then, the carbon-fiber chopped strands packed in the flexible container bag were measured  
30 for remaining ratio of original carbon-fiber chopped strands.

The results are shown in Table 1.

[0069]

#### Example 7

Three same, non-twisted, PAN-based carbon-fiber strands  
5 (Tenax STS 40-12K, a product of Toho Tenax Co., Ltd.) each  
composed of 12,000 single filaments were combined to obtain a  
carbon-fiber strand composed of 36,000 single filaments.  
Then, the carbon-fiber strand was subjected to the same  
operation as in Example 1 except that a twist was applied  
10 thereto, to obtain carbon-fiber chopped strands. The results  
are shown in Table 1.

[0070]

#### Example 8

Two same, non-twisted, PAN-based carbon-fiber strands  
15 (Tenax STS 40-48K, a product of Toho Tenax Co., Ltd.) each  
composed of 48,000 single filaments were combined to obtain a  
carbon-fiber strand composed of 96,000 single filaments.  
Then, the carbon-fiber strand was subjected to the same  
operation as in Example 1 except that a twist was applied  
20 thereto, to obtain carbon-fiber chopped strands. The results  
are shown in Table 1.

[0071]

#### Example 9

Five same, non-twisted, PAN-based carbon-fiber strands  
25 (Tenax STS 40-24K, a product of Toho Tenax Co., Ltd.) each  
composed of 24,000 single filaments were combined to obtain a  
carbon-fiber strand composed of 120,000 single filaments.  
Then, the carbon-fiber strand was subjected to the same  
operation as in Example 1 except that a twist was applied  
30 thereto, to obtain carbon-fiber chopped strands. The results

are shown in Table 1.

[0072]

#### Comparative Example 5

5 A non-twisted, PAN-based carbon-fiber strand (Tenax STS 40-12K, a product of Toho Tenax Co., Ltd.) composed of 12,000 single filaments was twisted continuously in the same manner as in Example 1, to obtain carbon-fiber chopped strands. The results are shown in Table 1.

[0073]

#### 10 Comparative Example 6

A non-twisted, PAN-based carbon-fiber strand (Tenax STS 40-24K, a product of Toho Tenax Co., Ltd.) composed of 24,000 single filaments was twisted and subjected to the same operation as in Example 1, to obtain carbon-fiber chopped  
15 strands. However, the carbon-fiber chopped strands had a high repose angle, of 32° because the number of single filaments was small.

[0074]

#### Comparative Example 7

20 Five same, non-twisted, PAN-based carbon-fiber strands (Tenax STS 40-48K, a product of Toho Tenax Co., Ltd.) each composed of 48,000 single filaments were combined to obtain a carbon-fiber strand composed of 240,000 single filaments. Then, the carbon-fiber strand was subjected to the same  
25 operation as in Example 1 except that a twist was applied thereto, to obtain carbon-fiber chopped strands. However, the number of single filaments was too large; the step of adhesion of sizing agent and the step of strand cutting were unstable; and it was impossible to obtain chopped strands  
30 having intended properties.

[0075] [Table1]

Table 1

|                       | Number of filaments | Twist (times/meter) | Sizing agent adhered                                             | Dmin (mm) | Dmax (mm) | Dmax/Dmin | L/Dmin | Remaining ratio of original carbon-fiber chopped strand | Bulk density (g/liter) | Repose angle |
|-----------------------|---------------------|---------------------|------------------------------------------------------------------|-----------|-----------|-----------|--------|---------------------------------------------------------|------------------------|--------------|
| Example 1             | 48,000              | 3                   | 5.0%                                                             | 1.97      | 2.18      | 1.11      | 3.05   | 83.3%                                                   | 458                    | 25°          |
| Example 2             | 48,000              | 6                   | 4.8%                                                             | 2.00      | 2.14      | 1.07      | 3.00   | 71.4%                                                   | 438                    | 28°          |
| Example 3             | 48,000              | 1                   | 5.4%                                                             | 1.88      | 2.73      | 1.45      | 3.19   | 74.2%                                                   | 461                    | 29°          |
| Example 4             | 48,000              | 30                  | 4.6%                                                             | 1.62      | 1.98      | 1.22      | 3.70   | 70.2%                                                   | 375                    | 30°          |
| Example 5             | 48,000              | 3                   | 3.0%                                                             | 1.83      | 2.45      | 1.34      | 3.28   | 75.0%                                                   | 464                    | 27°          |
| Example 6             | 48,000              | 3                   | 9.0%                                                             | 2.03      | 2.09      | 1.03      | 2.96   | 98.0%                                                   | 480                    | 28°          |
| Example 7             | 36,000              | 3                   | 5.1%                                                             | 1.63      | 1.84      | 1.13      | 3.68   | 92.0%                                                   | 447                    | 28°          |
| Example 8             | 96,000              | 3                   | 5.1%                                                             | 3.70      | 4.04      | 1.09      | 1.62   | 71.4%                                                   | 288                    | 29°          |
| Example 9             | 120,000             | 3                   | 5.0%                                                             | 4.50      | 7.56      | 1.68      | 1.33   | 70.3%                                                   | 210                    | 30°          |
| Comparative Example 1 | 48,000              | 0                   | 4.3%                                                             | 1.68      | 3.31      | 1.97      | 3.57   | 58.8%                                                   | 462                    | 34°          |
| Comparative Example 2 | 48,000              | 100                 | 4.2%                                                             | 1.34      | 2.47      | 1.84      | 4.48   | 57.2%                                                   | 100                    | 45°          |
| Comparative Example 3 | 48,000              | 3                   | 0.5%                                                             | 1.33      | 2.62      | 1.97      | 4.51   | 43.6%                                                   | 95                     | 53°          |
| Comparative Example 4 | 48,000              | 3                   | 14.2%                                                            | 1.53      | 2.34      | 1.53      | 3.92   | 100.0%                                                  | 570                    | 36°          |
| Comparative Example 5 | 12,000              | 3                   | 6.0%                                                             | 0.95      | 1.12      | 1.18      | 6.32   | 100.0%                                                  | 430                    | 32°          |
| Comparative Example 6 | 24,000              | 3                   | 5.8%                                                             | 1.34      | 1.55      | 1.16      | 4.48   | 96.3%                                                   | 442                    | 32°          |
| Comparative Example 7 | 240,000             | 3                   | Unstable steps made it impossible to obtain an intended product. |           |           |           |        |                                                         |                        |              |
| Example 10            | 48,000              | 3                   | 7.0%                                                             | 1.85      | 2.45      | 1.40      | 3.24   | 73.0%                                                   | 405                    | 28°          |
| Example 11            | 48,000              | 3                   | 3.0%                                                             | 1.83      | 2.45      | 1.34      | 3.28   | 77.0%                                                   | 385                    | 29°          |

[0076]

#### Example 10

An operation was made in the same manner as in Example 1 except that there was used, as a sizing agent, an acetone  
5 solution of a urethane-modified epoxy resin (Adeka Resin EPU-4-75X, a product of ADEKA Co., Ltd.), to obtain carbon-fiber chopped strands. The results are shown in Table 1.

[0077]

#### Example 11

10 An operation was made in the same manner as in Example 1 except that there was used, as a sizing agent, an aqueous dispersion of a polyurethane resin (Dispercoll U-54, a product of Bayer Co., Ltd.) to obtain carbon-fiber chopped strands. The results are shown in Table 1.

15 [0078]

#### Examples 12 to 22

Each 200 kg of the carbon-fiber chopped strands obtained in Examples 1 to 11 was packed in a flexible container bag which was openable at the bottom, and supplied  
20 to a pellet-producing step. That is, the package was hoisted by a crane; the bottom of the bag was opened; the carbon-fiber chopped strands were fed into a hopper of extruder at one time by an amount filling the whole capacity of the hopper.

25 Each of the carbon-fiber chopped strands obtained in Examples 1 to 11 had a low repose angle, 30° or smaller and had excellent flowability. Therefore, a large amount of the carbon-fiber chopped strands in the hopper caused no clogging of fluff and was supplied stably from the hopper to a meter.

30 [0079]

Comparative Examples 8 to 13

Each 200 kg of the carbon-fiber chopped strands obtained in Comparative Examples 1 to 6 was subjected to the same operation as in Example 12; that is, the strands of 200  
5 kg was packed in a flexible container bag which was openable at the bottom, and was supplied to a pellet-producing step.  
[0080]

Comparative Example 8

In the carbon-fiber chopped strands obtained in  
10 Comparative Example 1, there was no twist of carbon fiber; therefore, the  $D_{max}/D_{min}$  was large at 1.97. That is, the section of chopped strand was flat; therefore, the contact area between strands was large. As a result, the chopped strands had a repose angle  $34^{\circ}$  and had low flowability.  
15 Clogging of fluff occurred in the hopper and the stable supply of chopped strands into meter was impossible.  
[0081]

Comparative Example 9

The carbon-fiber chopped strands obtained in  
20 Comparative Example 2 had too large a twist of 100 times per meter; therefore, there was no impregnation of sizing agent into the inner portion of strand. Therefore, there was little bundling of fibers in strand. That is, the  $D_{max}/D_{min}$  was large at 1.84 and the remaining ratio of original bundles  
25 was low. The repose angle was  $45^{\circ}$  and the chopped strands had low flowability. Consequently, clogging of fluff occurred in the hopper and the stable supply of chopped strands into meter was impossible.  
[0082]

30 Comparative Example 10

In the carbon-fiber chopped strands obtained in Comparative Example 3, the amount of sizing agent adhered was small at 0.5 mass % and, therefore, there was no sufficient bundling of fibers. That is, the  $D_{max}/D_{min}$  was large at 1.97 and the remaining ratio of original bundles was low. The repose angle was  $53^{\circ}$  and the chopped strands had low flowability. Consequently, clogging of fluff occurred in the hopper and the stable supply of chopped strands into meter was impossible.

10 [0083]

Comparative Example 11

In the carbon-fiber chopped strands obtained in Comparative Example 4, the amount of sizing agent adhered was large at 14.2 mass % and, accordingly, the surface of chopped strand was not smooth. That is, the repose angle was  $36^{\circ}$  and the flowability was low. Clogging of fluff occurred in the hopper and the stable supply of chopped strands into meter was impossible.

In the kneading of resin and carbon-fiber chopped strands in extruder, the dispersion of carbon-fiber chopped strands in resin was inferior, making it impossible to obtain pellets of good quality.

[0084]

Comparative Example 12

25 In the carbon-fiber chopped strands obtained in Comparative Example 5, the number of carbon fiber single filaments used was small at 12,000. Accordingly, the chopped strands obtained had a small diameter. As a result, the ratio of fiber length (L) and minimum diameter ( $D_{min}$ ) was large at 6.32. That is, the contact area was large;

therefore, the repose angle exceeded  $30^{\circ}$  and the chopped strands had low flowability. Clogging of fluff occurred in the hopper and the stable supply of chopped strands into meter was impossible.

5 [0085]

Comparative Example 13

In the carbon-fiber chopped strands obtained in Comparative Example 6, the number of carbon fiber single filaments used was small at 24,000. Accordingly, the chopped  
10 strands obtained had a small diameter. As a result, the ratio of fiber length (L) and minimum diameter (Dmin) was large at 4.48. That is, the contact area was large; therefore, the repose angle was large at  $32^{\circ}$  and the chopped strands had low flowability. As a result, clogging of fluff  
15 occurred in the hopper and the stable supply of chopped strands into meter was impossible.

## Claims

[Claim 1]

A carbon-fiber chopped strand bundled by 1 to 10 mass % of a sizing  
5 agent composed of 30,000 to 120,000 carbon fiber single filaments, in which  
carbon-fiber chopped strand the ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter  
( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both of the section of chopped strand  
is 1.0 to 1.8, the fiber length (L) of chopped strand is 3 mm or more, the ratio  
( $L/D_{\min}$ ) of the fiber length (L) of chopped strand and the minimum diameter  
10 ( $D_{\min}$ ) of chopped strand is 4 or smaller.

[Claim 2]

The carbon-fiber chopped strand according to Claim 1, wherein the  
fiber length (L) of chopped strand is 3 to 10 mm.

[Claim 3]

15 The carbon-fiber chopped strand according to Claim 1 or Claim 2,  
wherein the mass per unit length of chopped strand is 0.8 to 8.0 g/m.

[Claim 4]

The carbon-fiber chopped strand according to any one of Claims 1 to  
3, wherein the repose angle of chopped strand is 30° or smaller.

20 [Claim 5]

A method for manufacturing a carbon-fiber chopped strand comprising  
twisting, by 0.5 to 50 times per meter, an untwisted carbon-fiber strand  
composed of 30,000 to 120,000 single filaments; then introducing into a sizing  
agent bath, followed passing through a grooved roller, and then drying with  
25 shape regulated, to adhere 1 to 10 mass % of the sizing agent to allow a carbon-  
fiber strand bundled; and then, cutting the carbon-fiber strand so that the fiber  
length (L) of chopped strand become 3 mm or more, the ratio ( $L/D_{\min}$ ) of the  
length (L) of chopped strand and the minimum diameter ( $D_{\min}$ ) of chopped  
strand become 4 or smaller.

30 [Claim 6]

An assembly of carbon-fiber chopped strands bundled by 1 to 10 mass % of  
a sizing agent each composed of 30,000 to 120,000 carbon fiber single filaments,

in each carbon-fiber chopped strand the ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both of the section of chopped strand is 1.0 to 1.8, the fiber length ( $L$ ) of chopped strand is 3 mm or more, and the ratio ( $L/D_{\min}$ ) of the fiber length ( $L$ ) of chopped strand and the minimum diameter ( $D_{\min}$ ) of chopped strand is 4 or smaller, in which assembly the remaining ratio of original carbon-fiber chopped strands original bundled is 70% or higher.

[Claim 7]

A package of carbon-fiber chopped strands, comprising carbon-fiber chopped strands packed in a flexible container bag wherein carbon-fiber chopped strand bundled by 1 to 10 mass % of a sizing agent each composed of 30,000 to 120,000 carbon fiber single filaments, in each carbon-fiber chopped strand the ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both of the section of chopped strand is 1.0 to 1.8, the fiber length ( $L$ ) of chopped strand is 3 mm or more, the ratio ( $L/D_{\min}$ ) of the fiber length ( $L$ ) of chopped strand and the minimum diameter ( $D_{\min}$ ) of chopped strand is 4 or smaller,

in which package the remaining ratio of original carbon-fiber chopped strands bundled is 70% or higher.

[Claim 8]

A method for manufacturing pellets each composed of a thermoplastic resin and a carbon fiber, which method comprising

feeding directly into a hopper from a flexible container bag, the carbon-fiber chopped strands bundled by 1 to 10 mass % of a sizing agent each composed of 30,000 to 120,000 carbon fiber single filaments, in which carbon-fiber chopped strands the ratio ( $D_{\max}/D_{\min}$ ) of the maximum diameter ( $D_{\max}$ ) and the minimum diameter ( $D_{\min}$ ) both of the section of chopped strand is 1.0 to 1.8, the length ( $L$ ) of chopped strand is 3 mm or more, the ratio ( $L/D_{\min}$ ) of the length ( $L$ ) of chopped strand and the minimum diameter ( $D_{\min}$ ) of chopped strand is 4 or smaller.

### **Abstract**

Disclosed is a carbon-fiber chopped strand, and a manufacturing method of the same. The carbon-fiber chopped strand is composed of single filaments composed of 30,000-  
5 120,000 carbon fibers, and a sizing agent content 1-10% by weight that bundles the single filaments; the ratio of maximum diameter ( $D_{max}$ ) in the cross section and minimum diameter ( $D_{min}$ ) is 1.0-1.8, a length along a fiber direction is 3-10 mm, and a repose angle of 10-30°.

10