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(54) **Carbon short fiber and process for preparing same.**

(57) Disclosed herein is carbon short fiber characterized in that the fiber is made of one of those consisting of pitch-type optically isotropic carbon fiber, pitch-type optically anisotropic carbon fiber and the composite of the two carbon fiber, and is cotton-like.

The carbon short fiber is cotton-like, curls and is twisted so that it possesses bulkiness, elasticity and stretchability. Accordingly, the fiber by itself or in combination with metal, ceramics and the like may be utilized in various fields as the material having excellent characteristics.

Also disclosed is a process for preparing same. The process attains considerable economic effects by elevating the productivity because the pitch may be directly spun to the fiber.

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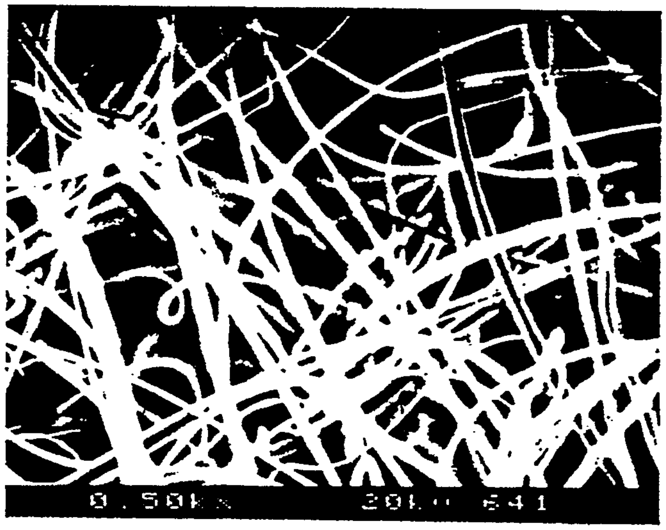
FIG. 3



Backgroung of the Invention

The present invention relates to cotton-like pitch-type carbon short fiber and a process for preparing same. Carbon fiber is broadly divided into PAN-based and pitch-type.

Currently, the PAN-based carbon fiber industrially manufactured by calcining polyacrylonitrile fiber under the specific conditious is utilized as high-strength material (HP type). Since, however, the PAN-based fiber possesses low carbon content, a decomposition gas may be envolved and the yield is as low as 50 to 55 %. Further, since the graphite structure in a high temperature is difficult to be developed, it is difficult to prepare carbon fiber with high modulus of elasticity though it is rather easy to prepare high strength products.

On the other hand, since the pitch-type carbon fiber is manufactured employing the pitch of coal and petroleum as raw material, the carbon content of spun fiber is as high as about 95% and the yield is also as high as 80 to 85 %. Further, since the PAN-based carbon fiber is excellently characterized in its physical property by the occurrence of high modulus of elasticity, its development has been rapidly advanced.

Even for the pitch-type carbon fiber, when pitch is melted, spun and calcined as it is, the carbon fiber with optical isotropy can be obtained. The carbon fiber thus obtained is utilized as broadly employed carbon fiber (GP products) for reinforcing material of a structure because it is inexpensive and produces constant strength. The carbon fiber bearing optical isotropy (carbonaceous mesophase) is to prossess high modulus of elasticity (HM type) by spinning pitch having all surface crystallizability because liquid crystals are arranged in the direction of a fiber axis in a shearing stress field during the spinning and huge graphite crystals can be produced by carbonizing the crystals.

Accordingly, product application being in conformity with these respective characteristics has been promoted; the carbon fiber simple substance is utilized as a filter, a catalyst, an electromagnetic shielder and the like; the carbon fiber in the composite material is utilized as reinforcing material of a matrix of a resin, a metal, carbon ceramics and the like broadly in the field of the universe, aviation, leisure, sports, industry and the like.

The research has been advanced for employing the carbon fiber in combination with engineering plastics as electronic parts, automobile parts and structural material.

In the case that the carbon fiber is employed as composite material, especially a large amount of the carbon fiber is employed as reinforcing material for structures, inexpensive material with high strength is required.

As mentioned earlier, the use of the pitch-type optically isotropic carbon fibr (GP products) in combination with cement as reinforcing material of walls of a multistory building has been promoted in place of asbestos because the said carbon fiber is inexpensive.

A variety of applications thereof as the reinforcing material of other structures have been investigated and put into practice. However, satisfactory results have not necessarily been obtained when the carbon fiber is employed as composite material in combination with plastics, a metal, ceramics and the like which requires high strength as a structural element because the strength of the carbon fiber is low.

On the other hand, the optically anisotropic carbon fiber possesses higher stretching strength and higher modulus of elasticity than the optically isotropic carbon fiber does, and may compensate more or less the above drawbacks in strength. At present, even the said anisotropic carbon fiber cannot satisfy the requests requiring material with higher fracture toughness in the field of electronics industry, automobile industry, space industry and the like. Situations are not matured in which the carbon fiber is broadly employed in viewpoint of the stability of quality, the mass production and the economical efficiency. As to a method for spinning the optically isotropic carbon fiber, the technology in connection with melted polymer and glass fiber such as a method for stretching by means of a rotary spinner and an air sucker and a vortex method is applied to the isotropic pitch. The diameter and the length of the fiber prepared by these methods are 10 to 20 µm and several tens to several hundreds mm, respectively. The fiber should be cut into small pieces so as to be employed as reinforcing material. Although, on the other hand, the anisotropic carbon fiber may be prepared according to one of the above-mentioned methods, most of the anisotropic carbon fiber is prepared as reinforcing material by forming roping fiber as lint by means of wind-up stretching from anisotropic pitch, cutting the said fiber into chopped fiber having a length of about 10 to 15 mm or less, and mixing the fiber with matrix material such as thermoplastics. This method includes a process of cutting the lint into smaller pieces having a fixed length.

When the carbon fiber is employed as composite material with the thermoplastics and a crack is generated in the composite material, the crack is likely to grow larger so as to invite a serious accident because the thermoplastics are ductile material while the carbon fiber for reinforcement which possesses large tensile strength and modulus of elasticity and low stretchability exhibits the behavior of britile material. It is a serious problem by which means the fracture toughness may be elevated. Primary factors of the facture of the plastics reinforced with the carbon fiber are the fracture of the atrix, the peeling between the matrix and the fiber, the breakage of the fiber, the draw-off of the fiber and the like, and the actual fracturee seems to occur by the combination thereof. Among them, the peeling between the matrix and the fiber and the draw-off of the fiber are the main factors.

The resons thereof may be that the carbon fiber is the material of high linearity and the surface mof the carbon fiber is so smooth that the bonding at the interface becomes insufficient, and so on.

When the carbon fiber is employed as a simple substance, it is necessary to provide much more surface area and much more space in a constant volume of a filter, a catalyst and a like, and the carbon fiber is molded with a binder for making a spacc after the fiber is woven as a net or piled like a mat. It is rather difficult to keep the space constant by employing the nets even if the woven ones are superposed. It is much more difficult to form a structural body provided with a constant cavity. The fiber is not at all employed in an application requiring an elastic structure.

Summary of the Invention

An object of the present invention is to provide cotton-like carbon short fiber.

Another of the present invention is to provide carbon short fiber possessing excellent compatibility with the matrix.

A further object of the invention is to provide carbon short fiber having the sufficient strength.

A still further object of the invention is to provide a process for preparing the above carbon short fiber.

A still further object of the invention is to provide a process for preparing the carbon short fiber requiring no cutting process and directly providing the fiber of the dimensions of chopped fiber by spinning.

The process for preparing the carbon short fiber according to the present invention can attain considerable economic effects by elevating the productivity because a cutting process which has heretefore been required for forming chopped strand is no longer required.

Although it has conventionally been considered that optically isotropic carbon fiber can be prepared only as widely employed products (GP products), the production cost for the preparation of pitch material or the like can be largely reduced according to the process of the invention because the pitch-type optically carbon fiber of which strength is equal to or larger than that of the pitch-type optically anisotropic carbon fiber can be obtained. Since the optically anisotropic carbon fiber of which strength is equal to or larger than that obtained by a conventional spinning method is obtained in this invention, the carbon fiber can be utilized as high strength composite material in combination with a metal, carbon, ceramics and the like for high strength and high accuracy structure element in the fields of electronics industry, automobile industry, space industry and the like.

Since the sectional shape of the fiber is deformative and the twist and curl are produced, the fiber by itself is cotton-like and prossesses bulkiness, elasticity and stretchability. Since the compatibility with the soft matrix is excellent when the fiber is employed for the manufacture of composite material, the peeling between the pitch-type carbon fiber and the matrix material is difficult to occur. Accordingly, the said carbon fiber is employed as composite material such as stretchable electroconductive material, elastic packing, engineering plastics and the like so that the high strengh composite material can be obtained which has not conventionally been obtained.

Brief Description of the Drawings

Fig.1 is a partial sectional view of an example of an apparatus employed a process for preparing carbon short fiber according to the present invention;

Fig.2 is a partial sectional view of another example of the apparatus;

Fig.3 is a 500 times microphotograph of the shape of the carbon fiber prepared in Example taken by a scanning electron microscope; and

Fig.4 is a 4000 times microphotograph prepared by further enlarging the fiber of Fig.3.

Detailed Description of the Invention

Pitch-type carbon short fiber of the invention is characterized in that the fiber is cotton-like, and is made of one of those consisting of pitch-type optically isotropic carbon fiber, pitch-type optically anisotropic carbon fiber and the composite of the two carbon fiber.

Further, a process for preparing carbon short fiber of the present invention comprises supplying at least one of those consisting of optically isotropic pitch and optically anisotropic pitch to a spinning apparatus, spinning the melted pitch while blowing the pitch through a blowing aperture by means of a gas pressure, making the pitch infusible and calcining it.

Since, the carbon short fiber of this invention prossesses the cotton-like shape as mentioned before, its conformability with the matrix is excellent and the fracture toughness against the peeling is elevated. In order to obtain such cotton-like carbon short fiber, it has conventionally been required that fiber which is once spun as lint is finished to the dimensions of the short fiber in the shape of a chopped strand through a cutting process. According to the present invention, however, the remarkable rise of the productivity can be attained because the raw material may directly be brought into a final shape.

Further, the fiber strength of the optically isotropic carbon fiber and of the optical anisotropic carbon fiber obtained by the process of the invention is about 1.4 to about 2.5 times stronger than the fiber strength obtained by a conventional spinning method so that the fracture toughness of composite material when the carbon fiber is brought into it can be elevated.

In case of the composite fiber comprising the optically isotropic carbon fiber and the optically isotropic carbon fiber, the conformability of the fiber with the matrix can be further improved because large twist and curl are produced due to the difference of their coefficients of thermal expansion. The fiber by itself can be employed as cotton-like carbon short fiber having certain growth since the twist and the curl provide the fiber with bulkiness and elasticity.

The pitch-type carbon short fiber of this invention can be prepared from such starting material as heavy oil, in general, coal tar, petroleum decomposition tar and stream cracker tar having in their respective molecules many aromatic six-membered ring structures. Although the most suitable material is selected from these materials considering purity and chemical composition, these materials may be pretreated by solvent extraction, heat modification and the like if no materials meeting the requirements are found. It is necessary, in general, to eliminate fine solids such as free carbon contained in the starting heavy oil. One method thereof is to dissolve the heavy oil into aromatic oil as anthracene oil or into such an organic solvent as quinoline to filter the fine solids. Another method is that, after meso carbon ultra-fine spheres are formed which sufficiently adsorb free carbon, fine particles of minerals and ultra-fine solids, the spheres are eliminated by extraction filtration. Optically isotropic pitch can be obtained after the pitch obtained by concentrating the above filtrate is secondary heat-treated and condensation-polymerised together with eliminating lighter substances for controlling a softening point.

On the other hand, optical anisotropic pitch can be obtained as follows. The pitch is diluted with tetrahydroquinoline to three to four times volume, and hydrogenated in a solvent at a temperature of 400 to 450 °C and an auto-generated atmosphere of 10 to 30 kgf/cm^2. After the pitch is filtrated and free carbon is sufficiently eliminated, the solvent is removed. The pitch is finally heat-treated at a temperature of 450 to 500 °C to obtain the optically anisotropic (mesophase) pitch. The mesophase pitch can be obtained by another process which comprises, in the manufacture of gasoline by means of fluid catalytic cracking of lighter oil of petroleum, thermally treating heavy tar (FFC decant oil) by-produced to form the mesophase and controlling a softening point by eliminating lighter substances.

The properties of carbon fibers prepared from thus obtained optically isotropic pitch and optically anisotropic pitch are different. When, in general, the optically isotropic pitch is spun to make carbon fiber, the graphite crystals in the fiber after carbonization become fine so that orientation in a direction of a fiber axis becomes bad. Said carbon fiber is named as broadly employed type (GP product) and generally its tensile strength is around 100 kg/mm^2 and its modulus of elasticity is around 5 ton/mm^2. In case of the optically anisotropic pitch, it is important to suitably control the orientation of the molecules as well as to suitably prepare the raw material pitch especially for obtaining the carbon fiber having high strength and high elasticity. The orientation is affected by a spinning temperature, a nozzle shape and the mlecular orientation control. Accordingly, the mechanical characteristics vary in a broad range according to the conditions. The tensile strength of the carbon fiber currently obtained may be 300 to 500 kg/mm^2 and the modulus of elasticity may be 30 to 70 ton/mm^2.

The modulus of heat expansion of the optically isotropic carbon fiber is 4 X 10^{-6}/K, while that of the optically anisotropic one 2 X 10^{-6}/K which is half of that of the former.

As mentioned earlier, the present invention can remarkably elevate the respective characteristics of the optically isotropic carbon fiber and the optically anisotropic carbon fiber, and provides the cotton-like pitch-type carbon short fiber which can , after spinning, be formed to final shaped for use by means of infusibilization and calcination.

Example

A preferred Example of this invention will be hereinafter described. However, the Example does not intend to restrict the present invention.

As pitch for spinning, two kinds of optically isotropic pitch having a softening point of 230 °C and containing 98 % of optically anisotropic pitch having a softening point of 268 °C were employed. A spinning apparatus shown in Fig.1 was employed in which the inner diameter of a blowing aperture 1 of pitch was 0.2 mm and the aperture diameter of a nozzle 2 for gas passage was 0.5 mm. After one of the optically isotropic pitch 3 or the optically anisotropic pitch 4 was introduced into a pitch reservoir 5 and the inside was replaced with a nitrogen gas, the pitch was heated and melted by means of a heater 6. After the pitch temperature reached to a predetermined temperature, nitrogen gases having the same pressure were introduced into the upper part of the pitch reservoir 5 and through a gas introduction pipe 7. Fibrous pitch discharged from the lower part of the spinning apparatus was collected. The collectedfibrous pitch was heated in air to 320 °C in the heating rate of 2°C per minute, and was maintened for 30 minutes for making the pitch infusible. The pitch was then carbonized at 1000 °C in the nitrogen stream, and was graphitized at 2600 °C in the argon stream.

One carbon fiber thus obtained and cut to a fiber length of 5 mm was sticked on a pasteboard, and the tensile strength was measured according to a single fiber method prescribed in Japanese Industrial Standard R7601. The diamter of the fiber was measured according to a laser diffraction method in the said Standart R7601.

The physical properties of the carbon fiber obtained in the various conditions by changing the kinds of pitch and the spinning conditions are summarized in the below Table.

As shown in the Table, the higher the pitch temperature and the gas pressure become, the thinner the fiber becomes and the shorter the fiber length becomes. Altrough the fiber length varies considerably in the same lot and the tendency of the fiber length cannot be absolutely described, the longest fiber length of Lot No.1-1 was about 50 mm.

Fig.3 is a photograph (magnification: 500 times) of the shape of the carbon short fiber of Lot No.2-2 in the Table taken by employing a scanning electron microscope. The fiber diameter is of various sizes and is not constant. Most of the fiber curls and is not linear. It is also observed in the other lots that fiber itself curls. Fig.4 is a 4000 times microphotograph of the fiber of the same lot for further investigating the fiber shape. As shown in this photograph, the sectional shape of the fiber is not a circle but an ellipse. The reason the fiber curls seems that the

	Lot. No.	Temp. of pitch (℃)	Gas pressure (kg/m²)	Temp. of calcination (℃)	Maxinum length of fiber (μm)	Strength (kg/mm²)	Elongation (%)	Modulus of elasticity (kg/mm²)
Optically isotropic pitch	1-1	390	6	1,000	9.6	136	2.0	6,800
		390	6	2,600	9.7	147	2.1	7,100
	1-2	420	10	1,000	7.4	153	1.9	8,000
		420	10	2,600	6.1	—	—	—
Optically anisotropic pitch	2-1	400	6	1,000	12.9	248	1.4	17,500
		400	6	2,600	11.3	447	0.9	50,000
	2-2	400	10	1,000	10.3	306	1.8	17,500
		400	10	2,600	13.0	448	1.1	41,000
	2-3	440	20	1,000	7.5	—	—	—
		440	20	2,600	7.2	—	—	—

sectional shape of the fiber is an ellipse or a flatter ellipse.

Since the curled fiber of which a diameter is not more than 10 μm is short, it is likely to become a mass. Its touch is soft, elastic and cotton-like. However, it is easily fibrillated and is readily decomposed to a single fiber in water.

The fiber shape is depressed and twisted, and randomly curls. The fiber is cotton-like and bulky so that, when a vessel having a fixed shape is filled with the fiber, the fiber is fixed therein by means of the elasticity of the fiber even if the fiber is not employed as a mat. Accordingly, the vessel filled with the fiber is confirmatively employed as a filter as it is. Rubber-like carbon fiber composite can be obtained which has not conventionally been obtained by making the composite comprising the fiber and elastic plastics, from which a packing or the like with high resistance to wear and elasticity can be prepared.

Complicated sectional shape other than the ellipse can be obtained in the process of the present invention for preparing the carbon short fiber by employing the spinning apparatus having various sectional shape of the pointed end of the spinning aperture and of the blowing aperture.

The composite carbon short fiber prepared by the combination of the optically isotropic carbon fiber and the optically anisotropic carbon fiber may be also obtained by means of the spinning apparatus provided with a partition plate 8 as shown in Fig.2.

Claims

1. Carbon short fiber characterized in that the fiber is made of one of those consisting of pitch-type optically isotropic carbon fiber, pitch-type optically anisotropic carbon fiber and the composite of the two carbon fiber, and is cotton-like.

2. A process for preparing carbon short fiber comprising supplying at least one of those consisting of optically isotropic pitch and optically anisotropic pitch to a spinning apparatus, spinning the melted pitch while blowing the pitch through a blowing aperture by means of a gas pressure, making the pitch infusible and calcining it.

FIG. 1

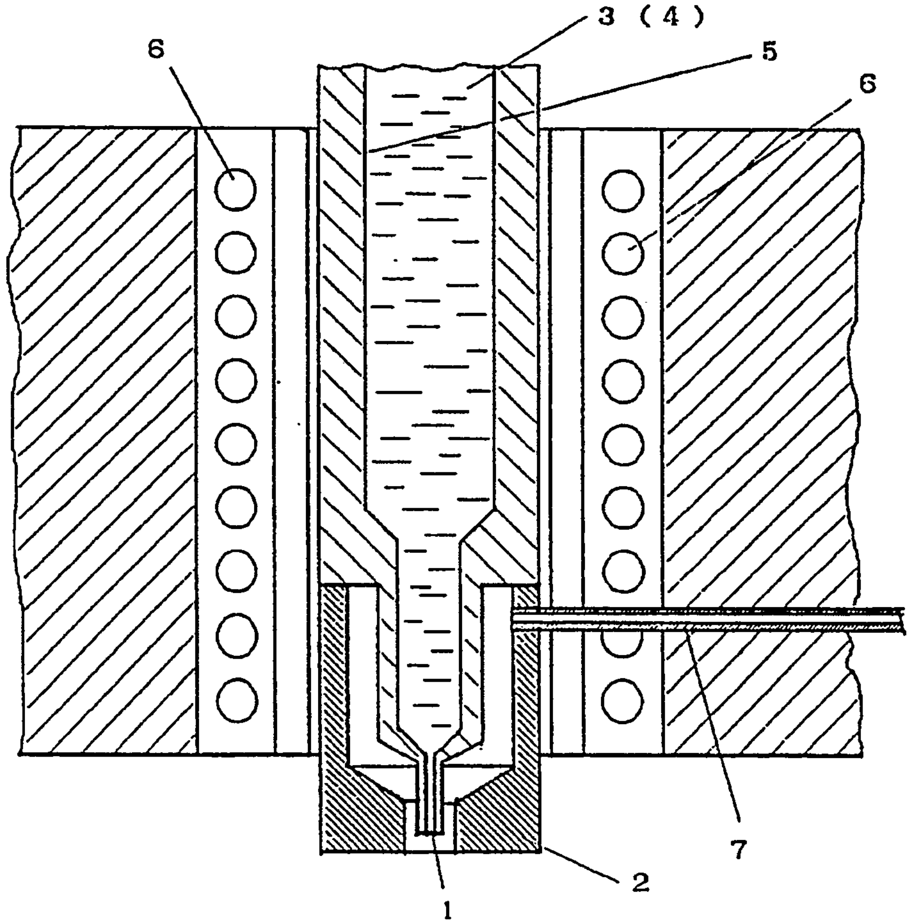


FIG. 2

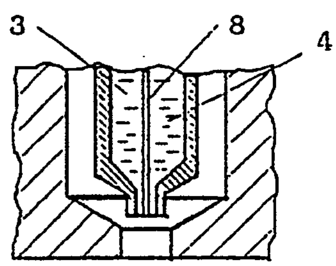


FIG. 3

FIG. 4