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METHOD OF PRODUCING CARBON FIBERS
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3 Claims

ABSTRACT OF THE DISCLOSURE

A method is provided for producing carbon fibers having a tensile strength of more than 150 kg./mm.² and a Young's modulus of more than 32,000 kg./mm.² by applying a vibrational energy to organic fibers under a tension in at least one of a drawing step for obtaining the precursor suitable for the production of carbon fibers, a pretreatment step for facilitating carbonization of the precursor, a carbonization step for substantially carbonizing the precursor and a graphitization step for graphitizing the carbonized fibers and for improving Young's modulus.

The present invention relates to a method of producing carbon fibers from organic fibers as a precursor. More particularly, it relates to a method of producing carbon fibers having a high Young's modulus.

The term "organic fibers" used herein includes rayon fiber, polyacrylonitrile fiber, vinylon fiber, pitch fiber and other synthetic fibers as well as natural fibers. That is, fiber-like organic substances, which can be carbonized or graphitized by a heat-treatment, can be used as a precursor for carbon fibers. At present, the above-mentioned fibers are practically used as the precursor.

Moreover, the term "carbon fibers" used herein means carbonaceous fibers and graphitic fibers.

A method for producing carbon fibers is generally as follows:

The organic fibers are previously heat-treated at a relatively low temperature of 150–300° C. in an oxidizing atmosphere such as air, oxygen, ozone, chlorine and the like or in a non-oxidizing atmosphere such as nitrogen and the like, or said fibers are impregnated or coated with a compound containing nitrogen or phosphorus or both and then heated at the above described temperature as a pretreatment, whereby the fibers are gradually thermally decomposed. Then, the thus treated fibers are heat-treated (carbonization) up to 1,000° C. in vacuo or in an inert gas atmosphere (non-oxidizing atmosphere) and further, if necessary, heat-treated (graphitization) up to a temperature of about 2,500° C. to 3,000° C. whereat crystal structure of graphite is formed. Besides, the organic fibers may be drawn in the presence of a heat medium such as steam and the like prior to said pretreatment.

The carbon fibers obtained by said method may be used as such and further they may be used as a reinforcing material for composite materials, in which synthetic resin or metal is used as a matrix to form an improved composite material, which is light but has a high mechanical strength.

The carbon fibers are often compared with glass fibers, asbestos and the like, but they are characterized by light weight, excellent heat resistance, good thermal conductivity, excellent lubricating property and high Young's modulus. By using carbon fibers having a particularly high Young's modulus, improved composite materials having a highest specific modulus can be obtained. Therefore, it is very important that the carbon fibers used for obtaining such composite materials have high strength and

Young's modulus. In order to obtain carbon fibers having such a high Young's modulus, an improvement of the above-described general method of producing carbon fibers has been proposed, wherein the organic fibers are heat-treated under a tension in the pretreatment step. In this improved method, however, when a load of 40 mg./d. is applied (the load applied on 100 fibers of 2.5 deniers is 10 g.), the length of the fibers shrinks 12% and the obtained carbon fiber shows a Young's modulus as low as 27,000 kg./mm.², while when a load of 160 mg./d. is applied (the load applied on 100 fibers of 2.5 deniers is 40 g.), the length elongates 36% and the obtained carbon fiber shows a Young's modulus of 40,000 kg./mm.². In such a process, a tow of 10,000 to 500,000 deniers is frequently used as a precursor for carbon fibers, so that in order to obtain the load of 160 mg./d., said tow must be subjected to a load of 1.6 kg. to 80 kg. It is very difficult to uniformly apply such a load to each fiber of the tow in the heat-treatment step, particularly in a carbonization or graphitization step. Furthermore, when such a large load is applied on long fibers uniformly and continuously, the fibers are liable to be broken and therefore such a process is not preferable.

An object of the present invention is to provide a method of producing carbon fibers having a uniform and high Young's modulus under a low load without applying a high load on the above mentioned organic fibers.

Such an object is accomplished by applying a vibrational energy to organic fibers in the axial direction or the transverse direction under a tension in a part or whole of a series of heat-treatment steps for converting the organic fibers into carbon fibers. According to the present invention, the tension must be applied in order to sufficiently transmit the vibrational energy to the fiber. This tension is preferred to be from 20 mg./d. to 120 mg./d. When the tension applied to the fiber is less than 20 mg./d., the combination with the vibrational energy is insufficient and a satisfactory effect in each step cannot be expected, while even if the tension is increased to more than 120 mg./d., the effect does not increase in proportion to the increment of the tension. The more preferable range of the tension is from 40 mg./d. to 100 mg./d. By applying the vibrational energy, carbon fibers having a more uniform and higher Young's modulus than that of carbon fibers obtained only by applying a high load, such as 160 mg./d. can be obtained under a low load, for example, 40 mg./d. to 100 mg./d. without applying the above described high load. As mentioned above carbon fibers having a high Young's modulus are obtained only by applying a load as high as 160 mg./d., but the merit of the present invention lies in that carbon fibers having a higher and more uniform Young's modulus can be obtained by applying the vibrational energy.

Particularly, according to the present invention carbon fibers having a high Young's modulus more than 60,000 kg./mm.² can be easily obtained under a relatively low load (e.g. 40 mg./d.) by subjecting the fibers to a heat treatment while applying vibrational energy. For instance, according to the present invention it has been found that Young's modulus of 2 to 3 times higher than that of well-known carbon fibers obtained under a high load can be attained.

In the present invention, the vibrational energy is applied in a heat-treatment step heating at a relatively low temperature of 150° C. to 300° C. (a pretreatment step), a heat-treatment step heating up to about 1,000° C. (carbonization step) and a heat-treatment step heating at a temperature of 2,500° C. to 3,000° C. (graphitization step). Furthermore, the vibrational energy is applied in a step wherein organic fibers obtained by a wet or dry spinning process are drawn in boiling water or steam of 100°

C. to 140° C. or a solvent such as polyethylene glycol, glycerine and the like heated at 100° C. to 180° C. to improve degree of orientation, whereby organic fibers suitable for production of carbon fibers are obtained. The steps for producing carbon fibers according to the present invention can be divided into the following four steps:

- (1) drawing step (step for obtaining the precursor suitable for the production of carbon fibers),
- (2) pretreatment step (step for facilitating carbonization of polyacrylonitrile fiber, pitch fiber and the like),
- (3) carbonization step (step for carbonizing substantially the precursor), and
- (4) graphitization step (final step for graphitizing the carbonized fibers and for improving Young's modulus).

According to the present invention, the vibrational energy may be applied over the whole steps or in any one of the above four steps. Furthermore, the vibrational energy may be applied over any two or three steps of the above described steps. The vibration is desirable to be applied over the whole steps, but the time for applying the vibrational energy can be optionally selected depending upon kind and properties of organic fibers to be used.

The effects obtained by applying the vibrational energy in each step for producing carbon fibers are as follows:

(1) By applying the vibrational energy in the drawing step, the fibers having a high elongation percentage, an improved degree of orientation and a fine diameter can be obtained, which are preferable for the production of carbon fibers.

(2) In the pretreatment step, organic polymeric fibers such as polyacrylonitrile fiber, pitch fiber and the like are softened at a temperature of about 200° C. to 300° C., so that if the vibrational energy is applied in such a stage, the drawing ratio increases, the diameter of the fiber becomes fine and at the same time the inner deficiency of the fiber such as void, flaw and the like is removed, whereby the drawing effect appears noticeably.

(3) The application of the vibrational energy in the carbonization step is also effective. Generally, the carbon fiber in the carbonization step has a cross-linked structure, so that the drawing is very difficult. However, when the vibrational energy is applied in accordance with the present invention, it is possible to draw the fiber and the strength and Young's modulus can be improved.

(4) The carbon fiber in the graphitization step is deformed as in a plastic at an elevated temperature above 2,500° C. and when the vibrational energy is applied, the drawing is carried out uniformly and smoothly and consequently the application of the vibrational energy has a remarkable effect for improving strength and Young's modulus in the obtained product.

The frequency of the vibrational energy to be used in the present invention is from 10 cycle/sec., preferably 30 cycle/sec. to 1,000,000 cycle/sec. In the case of less than 10 cycle/sec. or more than 1,000,000 cycle/sec, an appreciable effect for improving Young's modulus and uniformity is not obtained.

Means for applying the vibration includes a mechanical means, an electrical or electromagnetic means, a sonic means and the like.

Furthermore, there are the following methods for transmitting vibrational energy:

- (1) A load is suspended from one end of the fiber and a vibrator is connected to another end, and the fiber is subjected to an axial vibration during the heating step.
- (2) A load is suspended from one end of the fiber and another end of the fiber is fixed and a vibrator is contacted with the intermediate portion of the fiber to be heat-treated, whereby the fiber is subjected to a vibration.
- (3) In a continuous process wherein the fiber is extended between rollers and is heat-treated at the intermediate portion thereof, one or both of said rollers are subjected

to a vibration, which is transmitted to the fiber through the roller.

These methods may be optionally adopted insofar as the aimed purposes are the same.

According to the present invention, the duration for applying the vibrational energy is preferably from 5 minutes to 10 hours in each of the above steps for producing carbon fibers. Even in the case of less than 5 minutes, some effect can be attained, but the improvement of uniformity and properties of the fibers to be treated is not sufficient. Furthermore, in the case of more than 10 hours there is no advantage in view of an effect. Rather, when the vibration is applied for too long a period, the yarn breakage of the fiber to be treated occurs frequently, so that such an application is not preferable.

In general, the carbon fiber shows a higher strength as the diameter thereof decreases. Presumably, this is based on the fact that the diameter of the fiber is reduced by drawing and the like and consequently, the deficiency such as voids and the like decreases and at the same time fibrous molecules approach with each other and the degree of orientation is improved. The method of applying the vibrational energy to the fiber according to the present invention has a remarkable effect for considerably reducing the diameter of the fiber and such a method will contribute to the approach of fibrous molecules and the improvement of degree of orientation and consequently, carbon fibers having higher strength and Young's modulus are obtained.

The following examples are given in illustration of this invention and are not intended as limitations thereof.

EXAMPLE 1

A bundle of 100 polyacrylonitrile fibers, each of which having a fineness of 2 deniers, was suspended in a vertical electric furnace and a load of 16 g. (80 mg. per denier) was applied to the lower end of the bundle and then a vibration of 50 cycles/sec. was applied to the bundle by means of an electromagnetic vibrator in air while maintaining the temperature at 200° C. The variation of the fibers are shown in the following Tables 1 and 2.

TABLE 1.—ELONGATION OF FIBER DUE TO VIBRATIONAL ENERGY

Polyacrylonitrile fiber, treating time, hr.	Elongation (percent)	
	No. vibration	Vibration of 50 cycle/sec.
0.5.....	25.0	27.5
1.0.....	26.3	42.5
1.5.....	28.8	48.6
2.0.....	30.6	53.0
2.5.....	32.5	55.0
3.0.....	34.0	55.2
.....		
.....		
10.0.....	34.0	55.2

TABLE 2.—PROPERTIES OF FIBER TREATED AT 200° C. FOR 8 HOURS

	No vibration	Vibration of 50 cycle/sec.
Diameter of fiber after treated, μ	17.2	12.5
Reducing ratio based on original length of fiber, percent.....	14.4	37.8
Tensile strength, kg./mm. ²	13	22
Young's modulus, kg./mm. ²	630	880

Table 1 shows that the elongation of the fiber treated with vibration is 1.6 to 1.7 times higher than that treated without using vibration. Furthermore, Table 2 shows that the diameter of the fiber treated without using vibration is 17.2 μ , which is only a reduction of about 14%, while the diameter of the fiber treated with vibration is 12.5 μ which is a reduction of about 40% and the product treated with the vibration has more excellent tensile strength and Young's modulus than the product not treated with the vibration.

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Then, the fiber was graphitized in an inert gas atmosphere to obtain a result as shown in the following Table 3, in which the fiber treated with vibration was excellent in Young's modulus and particularly in tensile strength.

TABLE 3.—PROPERTIES OF FIBER HEAT-TREATED AT 2,700° C.

	No vibration	Vibration of 50 cycle/sec.
Diameter of fiber (μ)	10.8	7.2
Tensile strength (kg./mm. ²)	120	195
Young's modulus (kg./mm. ²)	29,000	58,000

EXAMPLE 2

Polyacrylonitrile fibers with a purity of 94% (fineness: 2 deniers, a bundle: 3,000 fibers), which had been obtained by extruding through nozzles and coagulating into filaments, drying and drawing 6 times their original length in hot water, were drawn in a steam of 110° C. under a tension of 100 mg./d. while applying a vibration of 10,000 cycles/sec. according to the present invention. In this case, the maximum drawing ratio was 3 times, by which the fibers were drawn 18 times their original length. For the comparison, when the drawing was carried out without using vibration under the same condition as described above, the maximum drawing ratio was only 2 times and the drawing ratio based on the original fibers was 12 times and in case of more than 2 times the drawing was impossible because yarn breakage occurred.

These fibers were heat-treated up to 250° C. under a tension of 40 mg./d. and then up to 1,000° C. at a rate of 50° C./hr. and finally up to 2,800° C. in about 2 hours to obtain carbon fibers having properties as shown in the following Table 4.

TABLE 4.—PROPERTIES OF FIBER TREATED AT 2,800° C

	Present invention	Control (no vibration)
Tensile strength (kg./mm. ²)	200	120
Young's modulus (kg./mm. ²)	42,000	26,000

EXAMPLE 3

Polyacrylonitrile fibers of 1,000 deniers were heat-treated in an electric furnace at 230° C. under a load of 40 mg./d. while applying a vibrational energy of 50 cycles/sec. The properties of fibers after carbonization at 1,200° C. and fibers after graphitization at 2,700° C., when applying the vibrational energy for 0.5, 1 or 2 hours, are shown in the following Table 5.

TABLE 5.—EFFECT OF VIBRATION TIME

	Vibration for—			No vibration
	0.5 hour	1.0 hour	2 hours	
Diameter:				
Treated at 230° C., μ	12.2	11.4	10.7	14.0
Carbonized at 1,200° C.	7.1	6.5	6.3	8.6
Graphitized at 2,700° C.	6.3	5.8	5.3	7.4
Tensile strength (kg./mm. ²):				
Carbonized at 1,200° C.	186	192	178	164
Graphitized at 2,700° C.	174	182	172	150
Young's modulus (kg./mm. ²):				
Carbonized at 1,200° C.	21,000	22,000	22,000	12,000
Graphitized at 2,700° C.	57,000	62,000	60,000	30,000

From the above table, it can be seen that in any case the application of the vibrational energy is considerably effective for reducing the diameter of fibers and improving Young's modulus.

In this example, the heat-treatment was continued without applying the vibration after the vibration was applied for the given time as described in Table 5. When the vibration was applied, length of the fiber elongated but when the vibration was not applied, the fibers shrunk and after heated at 230° C., about 10% of elongation was observed. Even the resulting carbon fibers applied the vibration only in the heat-treatment at 230° C. showed a Young's modulus of 60,000 kg./mm.².

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It can be seen from this example that the effect of vibration is obtained even if the vibrational energy is not applied over the whole steps for thermally decomposing the organic fiber.

EXAMPLE 4

A bundle of 900 viscose rayon filaments having 1,400 deniers, said viscose having a polymerization degree of 450, was heat-treated from 150° C. to 300° C. at a rate of 10° C./hr. in nitrogen atmosphere and then heat-treated up to 1,000° C. at a rate of 100° C./hr. under a tension of 50 mg./d. while applying a vibration of 15,000 cycle/sec. and further heat-treated at 2,800° C. The properties of the thus obtained carbon fibers are shown in the following Table 6.

TABLE 6

	Elongation (percent)	Tensile strength (kg./mm. ²)	Young's modulus (kg./mm. ²)
Present invention	6	150	32,000
Control (under the same condition without applying vibration)	0.5	80	24,000

EXAMPLE 5

A bundle of 900 viscose rayon filaments having 1,400 deniers, said viscose having a polymerization degree of 450, was heat-treated from 150° C. to 300° C. at a rate of 10° C./hr. and further from 300° C. to 1,000° C. at a rate of 100° C./hr. in nitrogen atmosphere and then heat-treated in a graphitizing furnace at 2,900° C. under a tension of 90 g. (65 mg./d.) while applying a vibration of 500 cycles/sec. The properties of the thus obtained carbon fibers are shown in the following Table 7.

TABLE 7

	Elongation (percent)	Tensile strength (kg./mm. ²)	Young's modulus (kg./mm. ²)
Present invention	28	186	45,000
Control (under the same condition without applying vibration)	10	105	22,000

What is claimed is:

1. In a method of producing carbon fibers having a Young's modulus of more than 32,000 kg./mm.² and a tensile strength of more than 150 kg./mm.² from organic fibers as a precursor comprising

- (a) drawing the precursor suitable for the production of carbon fibers,
- (b) subjecting the drawn precursor to a heat treatment in an oxidizing atmosphere,
- (c) carbonizing the oxidized precursor in a non-oxidizing atmosphere and further,
- (d) graphitizing the carbonized fibers, the improvement consisting of

applying a vibrational energy of from 10 cycles/sec. to 1,000,000 cycles/sec. to said precursor or fiber under a tension of from 20 mg./d. to 120 mg./d. in at least one of said steps (a), (b), (c) and (d).

2. The method as claimed in claim 1, wherein the time for applying the vibrational energy is 5 minutes to 10 hours.

3. The method of claim 1 wherein said vibrational energy is at least 30 cycles/sec.

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