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[54] **PROCESS FOR PRODUCING CARBON FIBER**

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[56] **References Cited**

UNITED STATES PATENTS

3,053,775	9/1962	Abbott	423/447
3,242,000	3/1966	Lynch	8/115.5
3,281,261	10/1966	Lynch	8/115.5
3,385,915	5/1968	Hamling	423/447
3,395,970	8/1968	Machell	423/447
3,403,008	9/1968	Hamling	423/447
3,468,841	9/1969	Corbiere et al.	264/182
3,495,940	2/1970	Stuetz	423/447
3,497,318	2/1970	Noss	423/447
3,500,482	3/1970	Lloyd et al.	423/447
3,505,445	4/1970	Leonard et al.	264/182
3,547,677	12/1970	Gentilromme et al.	264/29
3,592,595	7/1971	Gump et al.	423/447
3,656,882	4/1972	Riggs	8/115.5
3,677,705	7/1972	Ram et al.	264/DIG. 19
3,681,004	8/1972	Torrance	264/182
3,734,897	5/1973	Stoy	264/182
3,840,505	10/1974	Sato et al.	260/42.17

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[57] **ABSTRACT**

A high productivity process for producing high quality carbon fibers is presented. An acrylonitrile copolymer containing at least 85 mole % acrylonitrile, 0.03 – 11 mole % of at least one cross-linkable vinyl monomer and, if desired, other comonomers, is spun into fibers. The fibers are stretched, pyrolyzed in an oxidizing atmosphere, and further heat-treated in a non-oxidizing atmosphere to effect carbonization and graphitization. To enhance pyrolysis in oxidizing atmosphere, a pyrolysis catalyst is added to the acrylonitrile copolymer, such as ethylene diamine copper nitrate.

5 Claims, No Drawings

PROCESS FOR PRODUCING CARBON FIBER

RELATED APPLICATION

This application is a continuation-in-part application of U.S. Serial No. 206.118 filed Dec. 8, 1971 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a high productivity process for producing high quality carbon fibers, and more particularly to a process whereby an acrylonitrile copolymer comprising at least 85 mole % of acrylonitrile and 0.03 – 11 mole % of at least one cross-linkable vinyl monomer together with or without other comonomers is spun into fibers and then thermally converted into carbon fibers.

2. Description of Prior Art

Carbon fibers have heretofore been used as a reinforcing material for composite materials. For this application, it is desirable that the fibers used be characterized by high tensile strength, high rigidity and a homogeneous fibrous structure.

In order to produce a high modulus and high tensile strength carbon fibers, acrylic fiber precursors are placed under tension throughout the whole pyrolysis procedure, particularly in the step of pre-oxidation. This serves for preventing orientation relaxation of the molecules constituting the fiber from occurring so far as possible and, at the same time, for accelerating the growth of fibrils in the fiber.

The phenomenon of thermal-relaxation of the molecular orientation is a characteristic of most thermoplastic polymers. However the relaxation of molecular orientation is undesirable. Accordingly, it is necessary to maintain acrylic fibers under tension for a prolonged time in pre-oxidation pyrolysis. It is also required that carbonization pyrolysis should be affected by elevating the temperatures at a rate sufficiently gradual to eliminate molecular degradation. These requirements make it extremely difficult to continuously produce a high quality carbon fiber. The problem has been, therefore, as to how to improve the low level of productivity due to the prolonged pyrolysis reaction. It has been suggested to overcome this difficulty to accelerate the speed of pyrolysis by the addition of an oxidizing agent, a fire retardant or the like, such as ammonium phosphate, zinc chloride, hydrogen chloride, manganese dioxide, chromium trioxide, potassium chromate, etc. None of these agents, however, have proven to be completely satisfactory in accelerating pyrolysis.

It has also been suggested to prevent an uncontrolled pyrolysis in the pre-oxidation step by copolymerizing a reactive monomer, such as acrolein, butadiene or the like with acrylonitrile. However, the use of such monomers causes a deleterious effect on the polymerization reaction, and even if a copolymer is obtained, the use of such monomers has a deleterious effect on the spinning and stretching procedures. This method is therefore not considered to have practical applications.

It has also been proposed to use ammonium phosphate, a halogenated compound or the like as a fire-retardant for rayon precursors or poly-vinyl alcohol precursors. The fibers obtained by pyrolyzing these precursors, however, are liable to be amorphous in nature and unsatisfactory in strength and rigidity, so that this method is also unsuitable for practical applications.

SUMMARY OF THE INVENTION

Accordingly, it is one object of this invention to provide a process for producing high quality carbon fibers at high levels of productivity.

It is another object of this invention to provide a process whereby pyrolysis of acrylic fibers can be accelerated without deleteriously affecting molecular orientation which had been imparted to the fibers by stretching.

It is a further object of this invention to provide a technique for preparing high modulus and high tensile strength carbon fibers.

These and other objects have now herein been attained by the process, comprising admixing with acrylonitrile copolymer, which contains at least 85 mole % of acrylonitrile an 0.03 – 11 mole % of at least one cross-linkable vinyl monomer together with or without other comonomers, 0.0002 to 5.5 g atom, calculated as metal, per mole of the acrylonitrile copolymer, of at least one pyrolysis catalyst, spinning the acrylonitrile copolymer into fibers, stretching the fibers to 1.2 to 8.0 times original length, heat treating the fibers in an oxidizing atmosphere, and subsequently heat treating the fibers in a non-oxidizing atmosphere to complete carbonization and thereafter, if desired, graphitizing the fibers to produce a graphite fibers.

The cross-linkable vinyl monomer can be cross-linked by various cross-linking methods such as heat treatment, emission of electron beam, irradiation of ultra-violet ray or radio-active ray or the like. Ordinarily, however, it may be thermally cross-linked, intramolecularly and intermolecularly.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In this invention, an acrylonitrile copolymer containing at least 85 mole % of acrylonitrile, and at least one cross-linkable vinyl monomer is spun into fibers, stretched to between 1.2 and 8.0 times its original length, heated in an oxidizing atmosphere at a temperature of from 210° to 320°C, heated in a non-oxidizing atmosphere at a temperature of from 250° to 1200°C, possibly further heated at a temperature of from 1200° to 2000°C, to graphitize the fibers. In this invention, at least one pyrolysis catalyst is added with an acrylonitrile copolymer. As the pyrolysis catalyst, ethylene diameter copper nitrate, copper acrylacetonate, chromium acetylacetonate, copper acetate, copper powder, metal complex of copper sulfate and succinamide, metal complex of zinc acetate and ethylene diamine or metal complex of copper nitrate and ethyl l-glutamate is used. This catalyst is added 0.0002 to 5.5 g atom, calculated as metal, per mole of the copolymer. A mixture of the copolymer and the catalyst is dissolved in a solvent to make spinning solution. The solution is preferably heated at a temperature of from 90° to 130°C. for 1 to 85 minutes prior to the spinning. Fiber are spun from this solution, and the fibers are washed with water and then stretched to 1.2 to 8.0 times its original length. The stretched fibers are heated in air at a temperature of from 210° to 320°C., heated in a non-oxidizing atmosphere at a temperature of from 250° to 1200°C. to yield carbon fibers.

In this invention, an acrylonitrile copolymer contains one or more cross-linkable monomers, such as acrylic acid, methacrylic acid, itaconic acid, itaconic acid amide, N-methylol acrylamide, ethylene glycol dimethacrylate, ethylene glycol diacrylate, divinyl benzene, glycidyl methacrylate, ethyl benzylazilidine acrylate and diacetone acrylamide.

These cross-linkable comonomers are included in the copolymer in amounts of from 0.03 to 11 mole % based on the total monomers constituting the copolymer.

For example, when methylol acrylamide is used as the crosslinking compound, it should be used in amounts of from 0.05 to 2.5 mole % to provide suitable results. In most instances, the cross-linking compound should be used in amounts of at least 0.05 mole %, and preferably within the range of 0.05 mole % to 0.5 mole %.

If the copolymer is too highly cross-linkable, the stability of the spinning solutions will be quite low, and it will have a strong tendency toward gellation. The viscosity may increase undesirably and a heterogeneous phase may be formed. Moreover, if the polymer is too highly cross-linkable, the stretchability of the polymer may be too low and it may be difficult to provide fibers with a high degree of orientation.

Other non-cross-linkable vinyl monomers, one or more of which may be used together with the above cross-linkable monomers, include methyl acrylate, vinyl acetate, and sodium vinyl sulfonate.

Generally, by the effect of other non-crosslinkable vinyl comonomers included in the copolymer, spinability of the copolymer seems to be improved as compared with those of an acrylonitrile homopolymer or an acrylonitrile copolymer containing only acrylonitrile and a small amount of cross-linkable monomers. In order to obtain acrylonitrile fibers having high stretchability and high tensile strength, it is preferred to use an acrylonitrile copolymer having excellent spinability. A carbon fiber having high tensile strength and high modulus can be prepared from an acrylic fiber precursor having a high tensile strength.

It is quite desirable to use copolymers containing between 0 and 7 weight percent of the non-crosslinkable vinyl monomer, to enable the use of elevated temperatures during the pre-oxidation process and to enable a more rapid increase in temperature elevation.

In this invention, the pyrolysis catalyst may be used either in the form of fine metal powders, metallic ions or metal complexes dissolved or dispersed in the spinning solution. The metal or the metallic ions added to the copolymer may form a ligand complex compound combined with the functional groups in the polymer.

As compared with polymers containing only acrylonitrile, copolymers containing the pyrolysis catalyst have far more usefulness for the formation of carbon fibers. In particular, such modified copolymers are capable of providing carbon fibers having a remarkably orderly graphite crystal lattice orientation and excellent orderly crystal growth. The scattering of fine graphite crystal lattices found after pyrolysis of fibers comprising only acrylonitrile is not obtained when the catalyst copolymer is used.

As the range for enabling the fiber formation, it is preferable to use 0.0002 to 5.5 g atom per mole of the copolymer (calculated on the metal content) of the catalyst. Suitable catalytic action will not be found in the catalyst is used in amounts of less than 0.0002 g atom per mole of the copolymer. On the other hand, if the catalyst is added in concentrations more than 5.5 g atom per mole of the copolymer, fiber spinning becomes difficult and the fibrous quality becomes extremely deteriorated.

The polymer used in this invention is dissolved in a spinning solvent and is spun by wet, dry, or dry-wet spinning process. A finishing agent is not required and is not desired, since it may deleteriously affect adhesion.

If a wet spinning process is used, any solvent remaining in the fiber may be removed, after which the fibers are stretched, as abovementioned.

Suitable spinning solvents include dimethyl formamide, dimethylacetamide, dimethylsulfoxide, nitric acid, an aqueous solution of sodium ferrocyanate or potassium ferrocyanate, and an aqueous solution of zinc chloride and the like.

The acrylonitrile copolymer is dissolved, in one of the abovementioned spinning solvents so as to prepare a 16 to 32 weight % polymer solution (spinning solution).

In this invention, it is desirable, to avoid the formation of spinning distortion so far as possible, which may be caused by skin-core or void-crack and the distortion of the micro-structure. In order to prepare an acrylic fiber having a homogeneous structure without forming a skin-core structure, it is desired that fibers are obtained by extruding the spinning solution containing 16 to 32 weight % of the copolymer into a dry heated air stream or a dry heated inert gas stream at 210° to 310°C., whereby the fibers are dried through vaporization to 3 to 25 weight % residual solvent content. Alternatively, in case of wet-spinning technique, it is preferred that the concentration of the spinning solvent in the spinning bath may be heightened to as high as 45 to 88 weight % and spinning is conducted under usual wet spinning tension as much as 0.01 g/denier or more. Further, in wet-spinning technique, fibers are preferably formed by extruding the spinning solutions into a coagulating bath containing 35 to 45 weight % of a spinning solvent under a tension of 0.001 g/denier or less.

In conventional carbon fibers or graphite fibers, continuous multi-layers of highly oriented graphite crystal lattices are formed on the surface of the individual fibers. The mechanical characteristics of the carbon fibers or graphite fibers are mainly dominated by the characteristics of this skin layer, since the existence of voids and cracks in the skin layer are the primary structural defects of the fiber. The formation of the undesirable skin layer seems to be influenced by the fibrous structure of the acrylic fiber precursor, which, in turn, seems to be influenced by the oxidation conditions. This skin structure can be minimized by practicing some of the techniques of the present invention as described above.

The thus-obtained fibers are then stretched to orient the polymeric molecular chains. Such a stretching may be conducted in one or more steps. Stretching is conducted to 1.2 to 8 times original length in boiling water, super-heated steam or super-heated air.

Observation of the fibers by means of electron microscope indicates that the highly developed fiber fibrils are well arranged in the direction of the fiber axis and that the fiber fibrils are closely arranged.

Stretching, which can be conducted either before oxidation procedure, or at latest by the end of thermalsetting (thermal stabilizing), should be accomplished so as to provide a degree of molecular orientation of at least 0.45, as measured by infrared dichroism.

Acrylic fibers used in this invention preferably have a degree of molecular orientation of at least 0.45 and preferably from 0.45 to 0.84. The degree of molecular orientation is determined by the infrared dichroism obtained by comparing the magnitude of the infrared spectra of the fiber in the direction of the fiber axis with that of the spectra in the direction perpendicular to the fiber axis. Acrylonitrile polymers have a characteristic infrared absorption band at 2240 cm^{-1} of the $C \equiv N$ bond, which serves as a standard for the measurement of the respective magnitudes of infrared absorption. From this infrared dichroism, the molecular orientation can be calculated. Highly stretched acrylic fibers have a degree of molecular orientation of at least 0.45, and if the spinning and stretching are conducted idealistically, the degree of molecular orientation will approach about 0.84. Such fibers possess tensile strengths as high as 14 g/denier. When the infrared dichroism is not obtainable due to coloration, X-ray diffraction—$2\theta =$ 16—indicates that the orientation is 85 % more when molecular orientation is 0.45 or more.

There are various techniques for obtatining a molecular orientation of between 0.45 and 0.84. Preferably, fibers are stretched in warm water or boiling water to a high extent and then stretched further while heating at a temperature of from 120° to 210°C. The stretched fiber is then subjected to pre-oxidation.

In the pre-oxidation process, the stretched acrylic fibers are heat-treated in an oxidizing atmosphere. The heat-treatment is usually conducted at 210° to 320°C. If the fibers are colored so that the infrared dichroism measurement is rendered impossible, the molecular orientation degree should be 85 % or more according to X-ray diffraction measurement.

Pre-oxidation may be effected while stretching the fibers (precursors) in multi steps in an electric heating furnace, or by means of a Nelson's heating roller system.

Moreover, during the pre-oxidation process, shrinkage of 0–44 % occurring during the reaction may alternatively be permitted instead of stretching. When the extent of the shrinkage exceeds 44 %, the orientation of the graphite lattices of the carbon fibers and the graphite fibers to be obtained will be largely reduced, thereby preventing the formation of high strength and high rigidity carbon fibers. This shrinkage is caused partially by the relaxation of the fiber structure and the molecular structure, but is mainly due to the structural distortion resulting from the thermal deformation of the fiber structure.

Upon the completion of the oxidation procedure, the fibers are preferably charged into a mercury-sealed carbonizing furnace containing atmosphere of argon, nitrogen, carbon dioxide or the like. Carbonization is carried out while maintaining the fibers under a tension of 0.01 to 0.15 g/denier. The temperature in the carbonizing zone is elevated at a rate of 0.5° to 10°C./minute up to 800°C. The carbonized fibers may then be further pyrolyzed in a graphite furnace under an argon stream at temperatures of from 1200°C. up to 2000°C. to yield high quality graphite fibers.

In the graphitization treatments, the heating temperature should at least be 1200°C. If the temperature were lower than 1200°C, the growth and the orientation of the graphite crystal lattices could hardly be expected.

The characteristics of the carbon fibers obtained by the process of this invention are similar to those of conventional fibers, except that they possess higher strength and high rigidity characteristics, and display an excellent degree of homogeneity in fibrous structure, and a quite narrow tensile strength distribution. Accordingly, the carbon fibers of this invention are superior to conventional carbon fibers in the case of use as a material of construction, their dependability as a composite material or as a reinforcing material, etc.

Having now generally described the invention, a further understanding can be obtained by reference to certain specific Examples which are provided herein for purposes of illustration only. Unless otherwise indicated, all percents and parts are intended to be by weight.

EXAMPLE 1

23 Parts of acrylonitrile copolymer (ηsp: 0.205) comprising 95 mole % acrylonitrile, 3 mole % methyl acrylate, 1 mole % methacrylic acid and 1 mole % N-methylol acrylamide, was admixed with ethylenediamine-copper nitrate salt (0.04 g atom/per mole of the copolymer calculated on the copper metal content), and dissolved in 77 parts of dimethylformamide (DMF) to make a spinning solution. Before spinning, the spinning solution was heated to 120°C. for 30 minutes, so that the N-methylol group and the nitrile group were partially subjected to the ligand exchange reaction. The blue-green solution turned to red-brown. The temperature of the solution was decreased to 60°C., and the solution was extruded into a 65 % DMF aqueous solution to form fibers. The fibers were washed with water to remove the solvent. Thereafter, the fibers were stretched twice in boiling water, and after drying, further heat stretched 3 times as much as the original length at 160°C.

The fibers possessed superior fiber properties: the average fineness, 1.4 denier; the ultimate tensile strength, 4.0 g/denier; the ultimate elongation, 13.5%; and the Young's modulus, 98 g/denier. Its molecular orientation function according to the infrared dichroism was as much as 0.48. The fibers had a slightly yellow color. The freeness of the fiber was good.

In order to effect continuous heat treatment, the fibers were passed for 1 hour under a tension of 100 mg/denier through an electric heating tube furnace at a temperature of from 200° to 250°C. In this pre-oxidation reaction, structural stabilization due to cross-linking the ring formation reaction promoted by the added catalyst proceeded vigorously. The magnitude of the infrared absorption indicated that the nitrile group reacted to the extent of 85 %. Good anti-flaming properties were exhibited. The reaction shrinkage was 16% of the original length.

In a subsequent carbonizing reaction at 350°C to 700°C. in a pure argon steam, the temperature was gradually increased over 46 minutes up to 800°C. to complete carbonization, and then was gradually increased over 15 minutes up to 1000°C. to b **1,400°C.** to finally complete the pyrolysis. The properties of the thus-obtained carbon fibers were as follows:

The ultimate tensile strength: 29.5×10^3 kg/cm^2,
Young's modulus: 2.69×10^6 kg/cm^2,
the degree of orientation according to X-ray: $\pi =$ 87.4%, and
Standard deviation of the tensile strength: $\sigma = 18.3$ %.

The above-mentioned carbon fibers were pyrolyzed under tension for 5 minutes at 2,300°C. in a pure argon stream to obtain graphite fibers. The properties of the graphite fibers were as follows:

The ultimate tensile strength: 18.3×10^3 kg/cm^2,

Young's modulus: $4.21 \times 10^{6\ l\ ky/cm2}$, and
Specific gravity: 1.91 g/cc, and
the orientation of the graphite crystal lattices according to X-ray: $\pi = 91.6$ **5.**

EXAMPLE 2

To a spinning solution which contains 24 parts of acrylonitrile copolymer ($\eta sp = 0.189$) comprising 92 mole % acrylonitrile, 3 mole % vinyl acetate, 2 mole % acrylic acid amide and 3 mole % acrylic acid and 76 parts of dimethyl acetamide, a complex comprising copper sulfate and equivalent succinamide (0.03 g atom per mole of the copolymer calculated on the copper content) and copper acetylacetonate (0.05 g atom per mole of the copolymer calculated on the copper content) were added. This spinning solution was heated at 125°C. for 20 minutes, was extruded into a 35 % aqueous dimethyl acetamide solution under a tension of 0.001 g/denier or less to form fibers. The fibers were washed with water. After removing the solvent, the fibers were stretched in boiling water 3 times the original length; prior to drying, the fibers were then passed through steam at 124°C. and were further stretched 2.5 times the original length. The fibers were heat-treated at 180°C. to afford thermal dimensional stability. The fibers were comparatively well oriented, as seen from the measurement of molecular orientation degree according to the infrared dichroism which was as much as 0.52. The average fineness: 1.55 denier, the ultimate tensile strength: 4.65 g/denier, the ultimate elongation: 9.8 %, Young's modulus: 102 g/denier, and the copper content: 0.065 g atom per mole of the copolymer.

Pre-oxidation was affected by heat-treating the fibers at 225°C. for 40 minutes, under a tension of 98 mg/denier. Subsequently, by continuously increasing the temperature of the thus-obtained fibers over a period of 50 minutes up to 1,000°C. in a pure nitrogen stream in a high temperature furnace, carbonization was completed. The properties of the thus-obtained carbon fibers were as follows:

The ultimate tensile strength: 28.0×10^3 kg/cm^2,
Young's modulus: 2.03×10^6 kg/cm^2,
Specific gravity: 1.70 g/cc, and
the degree of crystal lattice orientation according to X-ray: $\pi = 87.1$.

The percentage of shrinkage of the carbon fibers were about 21 % of the original length.

EXAMPLE 3

A copolymer comprising 95 mole % acrylonitrile, 3 mole % acrylamide and 2 mole % itaconic acid, to which a metal complex comprising 1 mole zinc acetate and 2 moles ethylenediamine (0.02 g atom per mole of the copolymer calculated on the zinc content) was added, was dissolved in DMF to prepare 26 % DMF solution (spinning solution). This solution was heat-treated at 98°C. for 35 minutes. The slightly violet solution turned to a light reddish brown. This solution was extruded into an aqueous coagulate bath to form fibers. The fibers were stretched in boiling water to 5 times its original length, and were further stretched in steam at 120°C. 1.8 times. The molecular orientation obtained by means of infrared dichroism was 0.57. The average fineness of the fibers was 1.38 denier; the ultimate tensile strength, 6.7 g/denier; the ultimate elongation, 0.2 %; and the Young's modulus, 119 g/denier. When the fibers were heat-treated at 225°C. for 10 minutes, the fibers were completely stabilized into the state of excluding further thermal shrinkage. The percentage of shrinkage at this time was 11 %. When carbon fibers are prepared from such fibers, tension control to prevent the orientation relaxation of the molecular chains is not required. Thus, the fibers were treated without applying any tension from 235°C. for 12 minutes, and at 244°C. for 10 minutes to complete the reaction.

Subsequently, the temperature was increased in 93 minutes from 200°C. to 1300°C. in an argon stream to effect carbonization and graphitization. The various properties of the carbon fibers obtained were as follows:

The ultimate tensile strength: 32.0×10^3 kg/cm^2,
Young's modulus: 3.4×10^6 kg/cm^2, and
Specific gravity: 1.74 g/cc.

EXAMPLE 4

A copolymer comprising 95 mole % acrylonitrile, 3 mole % acrylamide and 2 mole % acrylic acid, to which a metal complex comprising 1 mole zinc acetate and 2 mole ethylenediamine (0.02 g atom per mole of the copolymer calculated on the zinc content) was added, was disloved in DMF to prepare a 26 % solution (spinning solution). This solution was heat-treated at 98°C. for 35 minutes. The slightly violet solution turned a light reddish-brown. This solution was extruded into a 78 % DMF aqueous solution at 25°C. to form fibers. The fibers were washed with water and stretched in boiling water to an extent of 2.3 times its original length. The average fineness of the fibers was 3.8 denier; the ultimate tensile strength, 1.9 g/denier; and the average ultimate elongation, 34 %. First, while further stretching the fibers to a total of 2.6 times its original length by a multi-step Nelson's roller heated at 185°C., the fibers were subjected to heat treatment in nitrogen stream at 226°C. for 10 minutes. Thereafter the pre-oxidation was continuously effected for 40 minutes in air up to 235°C. Subsequently, fibers were subjected to the heat treatment by increasing the temperature from 200°C. to 1000°C. in an argon stream to obtain carbon fibers having the physical properties as follows:

The ultimate tensile strength: 33.6×10^3 kg/cm^2,
Young's modulus: 2.8×10^6 kg/cm^2,
Specific gravity: 1.70 g/cc,
The orientation of the crystal lattices according to X-rays: $\pi = 84.2$;, and
Standard deviation of the tensile strength: $\sigma = 11.3$ %.

It is clear that the thus obtained carbon fibers are extremely strong and do not include significant areas of non-uniformity.

The acrylic fiber stretched by the Nelson's roller had such a highly oriented structure that 92 % of acrylonitrile molecules incorporated in the copolymer are oriented, as measured by X-ray just after stretching.

EXAMPLE 5

A copolymer comprising 95 mole % acrylonitrile, 3 mole % acrylamide and 2 mole % itaconic acid was dissolved in DMF. Into this solution was added a metal complex comprising copper nitrate and ethyl l-glutamate at a molar ratio of 1:2 (0.04 g atom per mole of the copolymer calculated on the copper content) to prepare a 26 % DMF solution (spinning solution) of the said copolymer. This solution was heated at 95°C. for 40 minutes. The heat-treated solution was extruded into a dry-hot air stream at 280°C. to form unstretched fibers. The unstretched fibers were stretched in boiling water to 7 times its original length, and further stretched to 2.5 times its stretched length in superheated steam at 128°C. to obtain highly oriented fibers. The molecular orientation function was 0.64; the ultimate tensile strength, 7.8 g/denier; the ultimate tensile elongation, 9 %; and the average fineness, 1.2 denier. First, the fibers were heat-treated for 10 minutes at 226°C. in an inert nitrogen stream, and then subjected to pre-oxidation in air at 235°C. for 40 minutes. Subsequently, the thus-treated fibers were heat-treated by increasing the temperature from 200°C. to 1,000°C. in an argon stream to obtain carbon fibers having the physical properties as follows:

The ultimate tensile strength: 34.8×10^3 kg/cm^2,
Young's modulus: 2.8×10^6 kg/cm^2,
Specific gravity: 1.71 g/cc, and
The orientation of crystal lattices according to X-ray: $\pi = 87.4$ %.
The shrinkage of the carbon fibers during pre-oxidation and carbonization was 9 %.
The carbon fibers are characterized in high tensile strength and high regidity.

EXAMPLE 6

23 Parts of the acrylonitrile copolymer (ηsp = 0.191) comprising 96 mole % acrylonitrile, 3 mole % acrylic acid and 1 mole % N-methylol acrylamide was dissolved in 77 parts of dimethyl acetamide to make spinning solution. Into this spinning solution was added chromium acetylacetonate in an amount of 0.13 g atom per mole of the acrylonitrile polymer (calculated based on metal), whereby was obtained a reddish violet spinning solution, which was heated at 98°C. for 40 minutes. The solution was then cooled to 55°C. Fibers were spun by extruding the solution into a 40 % aqueous dimethyl acetamide solution under a tension of 0.001 g/denier or less, and washed. The obtained unstretched fibers were stretched 6 times the original length in boiling water and further stretched twice in heated steam at 128°C. Fibers having monofilamentary denier of 1.2 were obtained. The molecular orientation function according to infrared dichroism of the thus obtained acrylic fibers (precursor for carbon fibers) was 0.56. The fibers were subjected to a cross-linking reaction which was effected at 220°C. for 30 minutes under a tension of 85 mg/denier. The crosslinking reaction was completed with the result of about 15 % fiber shrinkage. The fibers were no longer soluble in dimethyl acetamide or dimethyl formamide. They had lost thermal plasticity and exhibited no thermal shrinkage. The fibers were then pre-oxidized in air at 235°C. for 45 minutes and thereafter heated in nitrogen under free tension whereby the temperature was raised from 240°C. to 1200°C. in 90 minutes to complete carbonization reaction. The thus obtained carbon fibers possessed the following properties:

The ultimate tensile strength: 37.2×10^3 kg/cm^2,
Young's modulus: 1.82×10^6 kg/cm^2,
Specific gravity: 1.74 g/cc, and
The degree of orientation according to X-ray graphite crystal lattice: $\pi = 84.9$ %.
The above carbon fibers were further heat-treated in pure argon stream in a graphitization furnace. The graphite fiber heat-treated at 1550°C, for 30 minutes and that heat-treated at 2450°C. for one hour had the following properties.
The graphite fibers heat-treated at 1550°C.
The ultimate tensile strength: 31.5×10^3 kg/cm^2,
Young's modulus: 2.5×10^6 kg/cm^2,
Specific gravity: 1.78 g/cc, and
The degree of orientation according to X-ray graphite crystal lattice: $\pi = 88.3$ %.
The graphite fibers had been shrunk by 22 % as compared with the original length of the acrylic fibers.
The graphite fibers heat-treated at 2450°C.
The ultimate tensile strength: 22.7×10^3 kg/cm^2,
Young's modulus: 4.8×10^6 kg/cm^2,
Specific gravity: 1.94 g/cc, and
The degree of orientation according to X-ray graphite crystal lattice; $\pi = 93.3$ %.
The graphite fibers had been shrunk by 24 % as compared with the original length of the acrylic fibers.

EXAMPLE 7

The acrylic fibers for carbon fibers used in Example 6 were subjected to a crosslinking reaction similarly as shown in Example 6, but the reaction was conducted in nitrogen stream at 225°C. for 20 minutes under a tension of 105 mg/denier. The cross-linked fibers were thereafter pre-oxidized under the same condition as in Example 6 and then carbonized at a temperature up to 1200°C. The obtained carbon fibers had the properties as shown below. The shrinkage was 19 % as compared with the original length.

The ultimate tensile strength: 35.2×10^3 kg/cm^2,
Young's modulus: 1.94×10^6 kg/cm^2,
Specific gravity: 1.72 g/cc, and
The degree of orientation according to X-ray crystal lattice: $\pi = 85.2$%.

EXAMPLE 8

Into a dimethyl acetamide solution containing 26 weight % acrylonitrile copolymer (η sp = 0.184 in DMF) comprising 94 mole % acrylonitrile, 4 mole % sodium vinyl sulfonate, and 2 mole % N-methylol acrylamide, was added ethylenediamine copper nitrate in an amount of 0.08 g atom per mole of the copolymer (calculated as copper metal). This solution was heated at 95°C. for 5 minutes and then extruded into a 65 % aqueous dimethyl acetamide solution to form fibers. The fibers obtained were washed with water and thereafter stretched 8 times in boiling water. Subsequently, the fibers were passed through a tube furnace in air at 240°C. to be stretched twice. The stretched fibers showed a high degree of orientation as much as $\pi = 94.8$ % according to the X-ray measurement. After stretching, pre-oxidation of the fibers was effected which was completed after 45 minutes. Then, carbonization and graphitization of the fibers were completed by heating the fibers at 250°C. to 1700°C. in a nitrogen atmosphere. The fibers had been elongated by 84 % as compared with the original length of the acrylic fiber. The carbonized fibers were further heat-treated in a graphitization furnace in pure argon at 2600°C. The properties of the carbon fibers and the graphite fibers were as follows:

	Carbon fibers	Graphite fibers
The ultimate tensile strength (kg/cm^2)	36.1×10^3	28.0×10^3
Young's modulus (kg/cm^2)	2.8×10^6	4.3×10^6
Specific gravity (g/cc)	1.78	1.94
The degree of orientation according to X-ray graphite crystal lattice (π)	89.2%	94.0%

EXAMPLE 9

The acrylonitrile copolymer used in Example 5, copper acetate (0.08 g atom per mole of the copolymer calculated as copper metal) and copper powder for an electrode (the product of Merck Co., 0.08 g atom per mole of the copolymer) were well mixed in a mixer heated with steam and dissolved in dimethyl sulfoxide to prepare about 31.0 weight % spinning solution. Fibers were wet-spun by extruding said solution into 60 weight % aqueous dimethyl sulfoxide solution. After washing, the fibers were stretched 4 times in a water bath at 75°C. and further stretched twice in heated steam at 128°C. The thus obtained acrylic fibers had an average tensile strength of 4.2 g/denier, an average elongation of 17 % and a fineness of 1.48 denier. The molecular orientation degree measured according to infra-red dichroism was 0.51. The fibers were subjected to pre-oxidation treatment which was effected in air at 230°C. for 40 minutes under a tension of 62 mg/denier. Immediately thereafter, the fibers were passed through a high temperature furnace in argon atmosphere whose temperature was increased from 240°C. to 600°C. Subsequently, the fibers were further heat-treated at 1200°C.

The properties of the carbon fibers obtained were as shown below. Shrinkage of the fibers during pre-oxidation, carbonization, and graphitization was 21 % as compated with the original length of the acrylic fibers.

The ultimate tensile strength: 26.6×10^3 kg/cm^2

Young's modulus: 3.3×10^6 kg/cm^2

Specific gravity: 1.80 g/cc

The degree of orientation according to X-ray graphite crystal lattice: $\pi = 89.6$ %

What is claimed is:

1. A process for producing a carbon fiber which comprises:

a. admixing with a copolymer containing at least 85 mole percent of acrylonitrile and 0.03 to 11 mole % of at least one cross-linkable vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, itaconic acid amide, N-methylol acrylamide, ethylene glycol dimethacrylate, ethylene glycol diacrylate, divinyl benzene, glycidyl methacrylate, ethyl benzylazilidine acrylate and diacetone acrylamide; 0.0002 to 5.5 g atom, calculated as metal per mole of copolymer, of at least one pyrolysis catalyst selected from the group consisting of ethylene-diamine copper nitrate, copper acetylacetonate, chromium acetylacetonate, copper acetate, copper powder, metal complex of copper sulfate and succinamide, metal complex of zinc acetate and ethylene diamine, and metal complex of copper nitrate and ethyl l-glutamate;

b. spinning said copolymer into a fiber;

c. stretching said fiber to 1.2 to 8.0 times original length;

d. heat treating said fiber in an oxidizing atmosphere at a temperature of 210° to 320°C until a degree of molecular orientation is obtained of at least 85% by X-ray diffraction measurements; and

e. heat treating said fiber in non-oxidizing atmosphere at a temperature of 250° to 1200°C to effect carbonization.

2. The process of claim **1**, wherein said fiber is further graphitized at a temperature of 1200° to 2000°C.

3. The process of claim **1**, wherein said copolymer contains 0 to 7 % of non-cross-linkable monomer.

4. The process of claim **3**, wherein said non-cross-linkable monomer is selected from the group consisting of methyl acrylate, vinyl acetate, and sodium vinyl sulfonate.

5. The process of claim **1**, wherein a spinning solution containing said copolymer admixed with said pyrolysis catalyst is heated at a temperature of 90° to 130°C for 1 to 85 minutes prior to the spinning of said copolymer into a fiber.

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