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Kimmel et al.

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[54] **PROCESS FOR THE PRODUCTION OF CARBON FILAMENTS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 265,123, June 22, 1972, abandoned.

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[58] **Field of Search** ..... 264/29, 206, 210 F; 423/447, 265, 123, 448

[56] **References Cited**

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[57] **ABSTRACT**

An improved process is provided for the production of carbon filaments. A dry spun acrylic filament which is capable of absorbing water is provided in a water-laden form by contact with water at 20° to 90°C., the resulting water-laden filament thereafter is drawn in a heated gaseous atmosphere (e.g., saturated steam), is thermally stabilized, and is carbonized. In a preferred embodiment of the process, the dry spun acrylic filament contains about 5 to 30 percent by weight of a water-miscible spinning solvent which is replaced by water upon said contact prior to said drawing. The resulting acrylic filaments contain a highly microporous and fibrillar internal structure (as evidenced by small angle X-ray scattering intensity) which has been found to be beneficial when thermally converted to carbon filaments.

20 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF CARBON FILAMENTS

Cross-Reference to Related Application

This is a continuation-in-part of our U.S. Ser. No. 265,123, filed June 22, 1972, now abandoned.

Background of the Invention

Acrylic filaments have been formed via a variety of dry spinning and wet spinning processes in the prior art. Such acrylic filaments following drawings have been utilized, inter alia, as fibrous precursors which upon thermal treatment are capable of yielding carbon filaments. It has generally been recognized that the structure of the carbon filaments is influenced to some degree by the nature of the fibrous material which is thermally converted into the carbon filaments and by the processing conditions utilized during the thermal conversion. It has also been recognized that carbon filaments are known to possess an internal structure which is somewhat fibrillar in nature and that some micropores (i.e., microvoids) in addition to the usual structural flaws may be detected within the same. See, for instance, the article by R. Perret and W. Ruland appearing in *J. Appl. Cryst.*, Vol. 3, Pages 525–532 (1970), entitled "The Microstructure of PAN-Base Carbon Fibres".

In the search for high performance materials considerable interest has been focused upon carbon fibers. Industrial high performance materials of the future are projected to make substantial utilization of fiber reinforced composites, and carbon fibers theoretically have among the best properties of any fiber for use as a high strength reinforcement. Among these desirable properties are corrosion and high temperature resistance, low density, high modulus and high tensile strength. Carbon fiber reinforced composites are commonly formed by incorporating carbon filaments in a resinous or metallic matrix. Representative uses for carbon fiber reinforced composites include aerospace structural components, rocket motor casings, deep-submergence vessels and ablative materials for heat shields on re-entry vehicles, etc.

Heretofore, those material scientists interested in attempting to improve the internal structure of carbon filaments have directed their attention largely to the elimination of strength reducing flaws within the same. See, for instance, the article by J. W. Johnson and D. J. Thorne appearing in *Carbon*, Vol. 7, Pages 659–661 (1969), entitled "Effect of Internal Polymer Flaws on Strength of Carbon Fibres Prepared From an Acrylic Precursor", and the article by J. W. Johnson appearing in *Applied Polymer Symposia*, Vol. 9, Pages 229–243 (1969), entitled "Factors Affecting the Tensile Strength of Carbon-Graphite Fibres".

Commonly assigned U.S. Ser. No. 244,541, filed Apr. 17, 1972, of Michael J. Ram and John P. Riggs is directed to an acrylic filament having a highly fibrillar and dense internal structure formed during a specifically defined wet spinning process which is particularly suited for thermal conversion to a carbon filament.

The present invention provides a novel route to the improvement of carbon filaments. The acrylic filaments utilized in the present process possess an internal structure generally unlike that exhibited by acrylic filaments of the prior art and unlike that exhibited by the filaments of U.S. Ser. No. 244,541, and surprisingly have been found capable upon thermal treatment of yielding improved carbon filaments as discussed in detail hereafter.

U.S. Pat. No. 3,018,157 to Kovarik discloses a non-analogous process whereby the dyeing uniformity of a polyacrylonitrile filament is stated to be enhanced through the heat stretching of a water wetted filament.

It is an object of the invention to provide an improved process for forming carbon filaments.

It is an object of the invention to provide an improved process for forming a carbon filament which utilizes an acrylic precursor internal structure which has been found to be beneficial when thermally converted to a carbon filament.

It is an object of the invention to provide a process for forming carbon filaments which are capable of substantial crack diversion upon fracture.

It is an object of the invention to provide an improved process for forming carbon filaments which employs a highly oriented acrylic filament possessing a highly developed microporous and fibrillar internal structure.

It is another object of the invention to provide an improved process for forming a carbon filament having highly satisfactory strength properties even if accompanied by the presence of structural flaws such as commonly encountered in carbon filaments of the prior art.

These and other objects as well as the scope, nature, and utilization of the invention will be apparent from the following description and appended claims.

Summary of the Invention

It has been found that in a process for the production of a carbon filament from a dry spun acrylic filament selected from the group consisting essentially of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent acrylonitrile units and up to about 15 mol percent of one or more copolymerized monovinyl units which is capable of absorbing water, comprising thermally stabilizing said filament until non-burning when subjected to an ordinary match flame, and heating said stabilized filament in a non-oxidizing atmosphere at a temperature of at least about 1000°C. until a carbonaceous filament is formed which contains at least about 90 percent carbon by weight; improved results are obtained by contacting said dry spun acrylic filament prior to said thermal stabilization with water at a temperature of about 20° to 90°C. until said filament substantially becomes water-laden, and drawing the resulting water-laden acrylic filament while suspended in a heated gaseous atmosphere at a temperature of at least 100°C. to form an acrylic filament having a highly microporous and fibrillar internal structure which is particularly suited for thermal conversion to a carbon filament.

DESCRIPTION OF PREFERRED EMBODIMENTS

The acrylic filament which is employed in the process of the present invention is formed via dry spinning and is capable of absorbing water upon contact with the same. The acrylic filament may be formed by utilizing conventional acrylic dry spinning techniques wherein a solution containing the dissolved polymer is passed through a shaped extrusion orifice into an evaporative atmosphere in which the solvent is substantially evaporated. The dry spun acrylic precursor either inherently possesses a microporous internal structure or is capable of possessing such an internal structure upon contact

with water. For instance, dry spun acrylic filaments commonly possess a microporous internal structure upon washing with a non-solvent for the same. A microporous internal structure may be conveniently imparted to a dry spun acrylic filament containing residual spinning solvent upon contact with water. During such contact the spinning solvent is removed and a microporous internal structure is imparted to the dry spun acrylic filament.

In the process of the present invention the dry spun acrylic filament is provided in a water-laden form by contact with water at 20° to 90°C., and the resulting water-laden filament is thereafter drawn while suspended in a heated gaseous atmosphere (e.g., saturated steam). The after-processing of the dry spun acrylic filament results in the production of an acrylic filament having a highly microporous and fibrillar internal structure which is particularly suited for thermal conversion to a carbon filament.

In a preferred embodiment of the process the acrylic polymer is either an acrylonitrile homopolymer or an acrylonitrile copolymer which contains at least about 85 mol percent of acrylonitrile units and up to about 15 mol percent of one or more monovinyl units copolymerized therewith. An acrylonitrile homopolymer is particularly preferred. Suitable copolymers commonly contain at least about 95 mol percent of recurring acrylonitrile units and up to about 5 mol percent of one or more monovinyl units copolymerized therewith. Representative monovinyl units which may be incorporated in the acrylonitrile copolymers include styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like. The acrylic polymers may be formed by standard polymerization processes which are well known in the art. Minor quantities of preoxidation or graphitization catalysts may optionally be incorporated in the bulk acrylic polymer prior to spinning.

In a preferred embodiment the acrylic solvent utilized to form the spinning solution from which the acrylic filament is dry spun may be N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, or N-methyl-2-pyrrolidone. The particularly preferred solvents for use in the process are N,N-dimethylformamide, and N,N-dimethylacetamide.

The spinning solution may be prepared by dissolving sufficient acrylic polymer in the solvent to yield a solution suitable for extrusion containing from about 20 to 30 percent acrylic polymer by weight based upon the total weight of the solution. In a particularly preferred embodiment of the invention, the spinning solution contains the acrylic polymer in a concentration of about 24 to 27 percent by weight based upon the total weight of the solution. The low shear viscosity of the spinning solution preferably should be within the range of about 100 to 1000 poise measured at 100°C., and most preferably within the range of about 200 to 500 poise measured at 100°C. If the spinning solution low shear viscosity is much below about 100 poise measured at 100°C., spinning breakdowns commonly occur. If the spinning solution low shear viscosity is much above about 1000 poise measured at 100°C., extremely high spinning pressures are required and plugging of the extrusion orifice may occur.

In a preferred embodiment of the process wherein the spinning solvent is N,N-dimethylacetamide, the spinning solution additionally contains about 0.1 to 5.0 percent by weight based upon the total weight of the solution, and preferably about 0.5 to 2 percent by weight based upon the total weight of the solution of lithium chloride dissolved therein. The incorporation of lithium chloride serves the function of lowering and preserving upon standing the viscosity of the spinning solution. The desired solution fluidity and mobility are accordingly efficiently maintained even upon the passage of time. For instance, it has been found that a solution comprising 22 parts by weight acrylonitrile homopolymer, 2 parts by weight lithium chloride, and 76 parts by weight N,N-dimethylacetamide solvent commonly exhibits a relatively constant low shear viscosity of about 150 poise measured at 25°C. after standing for 250 hours. A solution containing an even lesser concentration of acrylonitrile homopolymer and no lithium chloride (i.e., 20 parts by weight polymer, and 80 parts by weight N,N-dimethylacetamide) tends to increase in viscosity upon standing and exhibits a low shear viscosity of about 1000 poise measured at 25°C. after about 2½ hours. The lithium chloride may be dissolved in the N,N-dimethylacetamide solvent either simultaneously with the acrylic polymer or before or after the acrylic polymer is dissolved therein. Minor quantities of preoxidation or graphitization catalysts may optionally be incorporated in the spinning solution.

The spinning solution is preferably filtered, such as by passage through a plate and frame press provided with an appropriate filtration medium, prior to dry spinning in order to assure the removal of any extraneous solid matter which could possibly obstruct the extrusion orifice during the spinning operation.

The spinning solution containing the fiber-forming acrylic polymer is extruded through a shaped orifice into an evaporative atmosphere to form a dry spun acrylic filament containing about 5 to 30 percent solvent by weight.

The temperature of the spinning solution at the time of its extrusion should be within the range of about 110° to 170°C., and preferably at about 140° to 160°C. In a particularly preferred embodiment of the process wherein the spinning solvent is N,N-dimethylformamide the spinning solution is provided at a temperature of about 145° to 150°C.

The extrusion orifice or spinneret utilized during the dry spinning may contain a single hole through which a single filament is extruded, and preferably contains a plurality of holes whereby a plurality of filaments may be simultaneously extruded in yarn or tow form. For instance, tows of up to 500, or more, continuous filaments may be formed. The spinneret preferably contains holes having a diameter between about 80 and 150 microns. Spinning or extrusion speeds of about 50 to 800 meters per minute (e.g., 100 to 500 meters per minute) may be employed.

Suitable evaporative atmospheres for the dry spinning zone include nitrogen, argon, helium, etc. The preferred evaporative atmosphere is nitrogen. The evaporative atmosphere is provided at a temperature sufficient to cause a substantial volatilization of the spinning solvent as the spinning solution is extruded, while retaining about 5 to 30 percent by weight solvent within the as-spun filament. The optimum temperature for the evaporative atmosphere will vary with the specific spinning solvent, the size of the extrusion orifice, the degree of gaseous circulation within the dry spinning column and the concentration of the fiber-forming acrylic polymer in the spinning solution, as will be apparent to those skilled in the art. Suitable temperatures

for the evaporative atmosphere commonly range from about 150° to 200°C. and preferably from about 180° to 195°C.

The volatilized solvent from the spinning solution may be recovered from the vapor stream leaving the dry spinning zone in accordance with conventional techniques.

In a preferred embodiment of the process, the resulting dry spun acrylic filament containing about 5 to 30 percent solvent by weight (e.g., 8 to 10 percent solvent by weight) is continuously passed from the dry spinning zone to a first drawing zone containing a saturated steam atmosphere provided at about 100° to 120°C., and most preferably at about 100°C. The saturated steam atmosphere is provided at a pressure of about 0 to 15 psig depending upon the temperature of the same. While passing through the first drawing zone, a longitudinal tension is exerted upon the acrylic filament sufficient to draw the same at a draw ratio of about 1.5:1 to 6:1 and preferably at a draw ratio of about 2:1 to 3.5:1 (e.g., 3:1) to form a moderately oriented acrylic filament containing a microporous internal structure. Some residual solvent may be lost during the drawing in saturated steam. The microporous internal structure imparted in the first drawing zone may be detected by analysis in a dark field optical microscope, small angle X-ray analysis, etc.

The resulting dry spun acrylic filament containing a microporous internal structure formed as heretofore described or any dry spun acrylic filament which is capable of absorbing water is contacted with liquid water maintained at about 20° to 90°C., and preferably at about 40° to 60°C. (e.g., 50°C.) wherein residual solvent present therein is substantially removed and replaced by water. As residual solvent is replaced by water, the microporous internal structure is enhanced, and micropores initially present therein are filled with water. If desired, however, the dry spun acrylic filament may have been previously washed free of solvent and already include a microporous structure which is capable of absorbing water upon contact. Such contacting is preferably conducted by passing the filament through a water bath, wherein the water-miscible solvent present therein (if any) is leached out. Suitable residence times while in contact with water commonly range from about 5 seconds to 5 minutes, and preferably from about 25 to 90 seconds depending primarily upon the concentration of solvent in the filament and the temperature of the water during contact. Longer residence times may be selected but generally yield no commensurate advantage. The solvent concentration is commonly reduced to a level below about 0.2 percent by weight based upon the weight of the fiber when in contact with water, and preferably reduced to a level below about 0.01 percent by weight. The microporous internal structure of the acrylic filament is preserved and the filament becomes water-laden, i.e., the micropores present therein are substantially completely filled with water.

The resulting water-laden dry spun acrylic filament next is drawn while suspended in a heated gaseous atmosphere at a temperature of at least 100°C. to form an acrylic filament having a highly microporous and fibrillar internal structure. In a preferred embodiment of the process wherein the solvent containing dry spun acrylic filament was previously drawn in a saturated steam atmosphere prior to contact with water, the present drawing zone may be termed a "second drawing zone". This drawing zone may be provided at a temperature of about 100° to 180°C. Suitable gaseous atmospheres for the drawing zone are steam, air, nitrogen, argon, helium, etc. A saturated steam atmosphere provided at about 100° to 120°C. is preferred. The saturated steam atmosphere may accordingly be provided at a pressure of about 0 to 15 psig depending upon the temperature of the same. The saturated steam atmosphere is most preferably provided at about 100°C. While passing through the drawing zone, the water-laden dry spun acrylic fibrous material preferably is drawn at a draw ratio of about 2:1 to 12:1. If the water-laden dry spun acrylic filament has been previously drawn, draw ratios of about 2:1 to 8:1 are preferred, and most preferably draw ratios of about 2:1 to 3.5:1. The exact draw ratio selected for optimum results will be influenced by the filament denier and by whether the water-laden acrylic filament has been previously drawn as will be apparent to those skilled in the art. For instance, particularly good results are achieved when an as-spun acrylic filament having a denier of about 8 is drawn in the first and second drawing zones to a total draw ratio of about 6:1 to produce a final acrylic filament having a denier of about 1 to 1.8.

During the drawing treatment heretofore described while the acrylic filament is water-laden the micropores present therein are elongated to form the desired fibrillar internal structure having elongated pores disposed between adjoining fibrils.

The process of the present invention is capable of producing oriented acrylic filaments having a crystalline orientation by wide angle X-ray analysis of 5 to 50 degrees and a highly fibrillar internal structure as evidenced by an equatorial small angle X-ray scattering intensity of at least 70 counts per second (e.g., 70 to 3000 counts per second) at a $1/d$ value of 5×10^{-3} $A^{(-1)}$, and preferably of at least 180 counts per second (e.g., 180 to 500 counts per second).

For a description of how crystalline orientation of the filaments may be determined by wide angle X-ray analysis see the article by H. G. Ingersoll appearing in Volume 17 of the *Journal of Applied Physics*, Page 924 et seq (1946).

The determination of the equatorial small angle X-ray scattering intensity of the filament at a $1/d$ value of 5×10^{-3} $A^{(-1)}$ may be carried out employing a Kratky camera and conventional X-ray analysis techniques. See, for instance, the article by O. Kratky, G. Porod, and Z. Scala appearing in Volume 13 of Acta Physica, page 76 et seq (1960); the article by O. Kratky, I. Pilz, and P. F. Schmitz appearing in Volume 21 of the *Journal of Colloid and Interface Science*, page 24 et seq (1966); and the treatise by L. E. Alexander entitled "X-ray Diffraction Methods in Polymer Science", Wiley-Interscience (New York, 1969). See particularly the above treatise page 107 et seq for a discussion of the Kratky camera, and page 327 et seq for a discussion of small angle X-ray scattering in dense systems.

More specifically, a Kratky small angle camera is employed which is provided with proportional counter radiation measurement and electronic step scanning programing. The acrylic filament undergoing examination is inserted in a 1 mm. capillary tube and is aligned parallel to and centered in a line X-ray beam of the Kratky camera. The filament may be exposed to nickel filtered CuKα radiation, and the scattered intensity measured by use of a proportional counter with pulse height dis-

crimination. For example, the filament sample may be positioned 210 mm. from the exit slit, an entrance slit utilized having a height of 30 microns, and an exit slit utilized having a height of 75 microns. The scattering intensity is measured as a function of $S = 1/d = (2 \sin\theta/\lambda)$, where θ = the scattering angle, and $\lambda = 1.542$ A (value for CuKα radiation) employing a step scanning program. The attenuation of each sample is measured with an auxiliary standard as discussed in the article appearing in the *Journal of Colloid and Interface Science* referred to above which allows for normalization of the scattering intensity. The measured scattering intensity at $S = 1/d = 5 \times 10^{-3}$ A$^{(-1)}$ is divided by the sample attenuation factor to give the value designated as the equatorial small angle X-ray scattering intensity.

The acrylic filaments which are produced upon drawing form the subject matter of our U.S. Ser. No. 265,384, filed June 22, 1972 (now abandoned), entitled "Improved Acrylic Filaments Which Are Particularly Suited for Thermal Conversion to Carbon Filaments".

The drawn acrylic filaments may be plied to form yarns or tows of increased total denier as will be apparent to those skilled in the art prior to a thermal conversion to form improved carbon filaments. The resulting drawn acrylic filaments may be thermally converted to improved carbon filaments through the utilization of thermal processing known to those skilled in the art. The drawn filaments first are thermally stabilized and then are carbonized.

The stabilization treatment renders the acrylic filaments nonburning when subjected to an ordinary match flame while retaining their original fibrous configuration essentially intact. The stabilization reaction may be conducted by heating the acrylic filaments at moderate temperatures in accordance with techniques known in the art. Such a stabilization procedure is commonly conducted in the presence of oxygen and results in the formation of a cyclized and preoxidized product which exhibits a thermal stability not exhibited by the unmodified acrylic filaments. While it is possible that the stabilization reaction be conducted on a batch basis, it is preferable that the stabilization reaction be conducted on a continuous basis. Catalyzed stabilization reactions optionally may be selected. The exact stabilization temperatures employed will vary with the chemical composition of the acrylic filaments. Representative stabilization procedures are described in commonly assigned U.S. Pat. Nos. 3,508,874; 3,539,295; 3,592,595; 3,632,092; 3,656,882; 3,656,883; 3,708,326 and 3,729,549, which are herein incorporated by reference. Other stabilization procedures capable of imparting thermal stability to the acrylic filaments may be selected.

The stabilized acrylic filaments are converted to carbon filaments by thermal treatment at a more highly elevated temperature of at least about 1000°C., e.g., 1000° to 2000°C., or more, in a non-oxidizing atmosphere. Preferably inert atmospheres such as nitrogen, argon and helium are employed. The stabilized acrylic filaments are subjected to such highly elevated thermal treatment until carbon filaments containing at least 90 percent carbon weight are formed, and preferably until carbon filaments containing at least about 95 percent carbon by weight are formed. In a more particularly preferred embodiment, carbon filaments containing at least 98 percent carbon are formed. Upon carbonization, the acrylic filaments produced in the present process are capable of yielding the carbon filaments which form the subject matter of commonly assigned U.S. Ser. No. 244,544, filed Apr. 17, 1972 of Michael J. Ram and John P. Riggs, entitled "Improved Carbon Filaments Capable of Substantial Crack Diversion during Fracture". The subject matter of this copending application, as well as that of the other applications referred to herein, is incorporated herein by reference.

The following examples are given as specific illustrations of the process of the present invention. It should be understood, however, that it is not essential that the process be carried out employing the exact conditions set forth in the examples.

EXAMPLE I

Twenty-five parts by weight of polyacrylonitrile homopolymer and 75 parts by weight of N,N-dimethylformamide are slurried at −20°C. for 2 hours by use of a stirred vessel. The slurry is heated to a temperature of 95°C. over a period of 90 minutes where it is mixed with agitation for 2 hours. The solution while at 95°C. is passed through a conventional filter press in order to remove any solid contamination. The low shear viscosity (Brookfield) of the resulting spinning solution after degassing is found to be about 300 poise measured at 100°C.

The resulting spinning solution is provided at a temperature of 95°C. in a holding tank while under an atmosphere of nitrogen. The solution is fed from the holding tank to the spinneret provided at the top of the dry spinning column at a rate of 20 lbs. per hour. The dry spinning column has a length of approximately 21 ft. The spinneret includes a circle of 160 holes each having a diameter of 100 microns, and is provided at jet face temperature of 145°C.

A preheated stream of nitrogen is continuously introduced into the top of the dry spinning column at a rate of 17 standard cubic feet per minute, and is withdrawn from the bottom of the dry spinning column together with volatilized N,N-dimethylformamide. The nitrogen temperature at the jet face is 195°C. The temperature of the nitrogen evaporative atmosphere throughout the dry spinning column ranges from 180° to 195°C. Wall heaters are provided within the spinning column which aid in maintaining the elevated temperature of the nitrogen evaporative atmosphere. The as-spun denier of each resulting filament is about 9 dpf.

The resulting bundle of as-spun acrylonitrile homopolymer filaments is continuously withdrawn from the bottom of the dry spinning column at a rate of 200 meters/minute, and the filaments thereof include residual N,N-dimethylformamide in a concentration of about 9 percent by weight.

The bundle of as-spun acrylonitrile homopolymer filaments is continuously passed from the dry-spinning column to a first drawing zone which is provided with saturated steam at 100°C. The first drawing zone consists of a tube having a length of 2 feet in which the filaments are axially suspended. A pair of skewed rolls is positioned outside each end of the tube containing the steam atmosphere and exerts a longitudinal tension upon the bundle of filaments passing through the tube. The filaments are drawn at a draw ratio of 3:1 to form acrylonitrile filaments exhibiting a microporous internal structure. The drawn bundle of filaments is taken up on a bobbin at a rate of 600 meters/minute.

The bundle of microporous acrylonitrile homopolymer filaments next continuously is passed from the

bobbin at a rate of 5 meters/minute through a water bath maintained at 50°C. The bundle is immersed therein while at a constant length for a residence time of about 60 seconds. While present in the water bath, the residual N,N-dimethylformamide solvent is removed from the filaments and replaced by water.

The bundle of water-laden acrylonitrile homopolymer filaments next is passed at a rate of 5 meters/minute from the water bath to a second drawing zone which is provided with saturated steam at 100°C. The second drawing zone consists of a tube having a length of 2 feet in which the filaments are axially suspended. A pair of skewed rolls is positioned outside each end of the tube containing the steam atmosphere and exerts a longitudinal tension upon the bundle of filaments while passing through the tube. The filaments are drawn at a draw ratio of 2.2:1. The drawn filaments are taken up on a bobbin at a rate of 11 meters/minute and are dried.

These filaments possess a dogbone shaped cross-sectional configuration, a denier per filament of 1.32, an average single filament tensile strength of 4.43 grams per denier, an average single filament initial modulus of 127 grams per denier, an elongation of 9.58 percent, and a crystalline orientation by wide angle X-ray analysis of 20 degrees. More importantly, these filaments exhibit a highly microporous and fibrillar internal structure as evidenced by an equatorial small angle X-ray scattering intensity of 275 counts per second at a $1/d$ value of 5×10^{-3} $A^{(-1)}$, and are particularly suited for thermal conversion to carbon filaments.

See FIG. 1, and FIG. 3 of our U.S. Ser. No. 265,384, filed June 22, 1972, entitled "Improved Acrylic Filaments Which Are Particularly Suited for Thermal Conversion to Carbon Filaments" which illustrate the resulting acrylic filaments when examined under a scanning electron microscope and under a dark field optical microscope.

Five of the drawn filament bundles next may be plied to form a continuous length of acrylonitrile homopolymer fibrous material consisting of 800 continuous filaments. This resulting continuous length next may be subjected to a brief thermal pretreatment in accordance with the teachings of commonly assigned U.S. Ser. No. 260,341, filed June 6, 1972 (now abandoned). More specifically, the continuous length is passed continuously through an oven provided with an air atmosphere at 195°C. for a residence time of about 240 seconds while maintaining the longitudinal tension thereon so that 10.5 percent shrinkage in length takes place.

The continuous length of thermally pretreated acrylic fibrous material next may be passed for about 120 minutes through a multiple roll oven provided with an air atmosphere at 266°C. While passing through this oven the acrylic fibrous material is thermally stabilized and is rendered black and non-burning when subjected to an ordinary match flame. The resulting stabilized fibrous material retains its original fibrous configuration essentially intact, and contains a bound oxygen content of about 10.1 percent by weight when subjected to the Unterzaucher analysis.

The continuous length of stabilized filaments next may be converted to improved carbon filaments by passage through an Inductotherm induction furnace utilizing a 20 KW power source. The induction furnace comprises a water cooled copper coil and a hollow graphite tube suspended within the coil having a length of 38 inches and an inner diameter of 0.75 inch through which the continuous length of stabilized filaments is continuously passed. The copper coil which encompasses a portion of the hollow graphite tube is positioned at a location essentially equidistant from the respective ends of the graphite tube. An inert atmosphere of nitrogen is maintained within the induction furnace. Air is substantially excluded from the induction furnace by purging with nitrogen. The continuous length of stabilized filaments is passed through the induction furnace at a rate of about 3 inches per minute. A longitudinal tension of 0.2 gram per denier is exerted upon the continuous length of fibrous material as it passes through the induction furnace. The fibrous material is at a temperature of about 150°C. as it enters the induction furnace and is raised to a temperature of 800°C. in about 150 seconds, and from 800°C. to 1500°C. in about 200 seconds where it was maintained at 1500°C. ±25°C. for about 48 seconds.

The resulting carbon filaments contain in excess of 96 percent carbon by weight, and are found to possess an average flaw size of 1.7 microns and a mean apparent fracture surface energy of 55 joules per square meter. The average flaw size and the mean apparent fracture surface energy are determined as described in copending U.S. Ser. No. 244,544, filed Apr. 17, 1972.

The resulting carbon filaments additionally exhibit a specific gravity of about 1.63, a denier per filament of 0.63, an average single filament tensile strength of 15.8 gpd, an average single filament Young's modulus of 1818 gpd, and an elongation of 0.87 percent.

EXAMPLE II

Example I is repeated employing another embodiment of the process of the present invention. More specifically, the initial drawing in the first drawing zone is omitted, and the bundle of water-laden filaments is drawn to approximately the same total draw ratio in the second drawing zone containing saturated steam.

Following dry spinning the bundle of as-spun N,N-dimethylformamide containing filaments is collected upon a bobbin, and is subsequently passed through the water bath wherein the N,N-dimethylformamide is removed and replaced by water to form acrylonitrile homopolymer filaments having a microporous internal structure.

The bundle of water-laden filaments is fed into the second drawing zone at a rate of 5 meters/minute and is withdrawn from the second drawing zone at a rate of 30 meters/minute. The filaments are drawn at a draw ratio of 6:1.

The filaments possess a dogbone shaped cross-sectional configuration, a denier per filament of 1.42, an average single filament tensile strength of 3,95 grams per denier, an average single filament initial modulus of 94.6 grams per denier, an elongation of 12 percent, and a crystalline orientation by wide angle X-ray analysis of 25 degrees. More importantly, these filaments exhibit a highly microporous and fibrillar internal structure as evidenced by an equatorial small angle X-ray scattering intensity of 170 counts per second at a $1/d$ value of 5×10^{-3} $A^{(-1)}$, and are particularly suited for thermal conversion to carbon filaments. The filaments possess a less highly developed microporous and fibrillar internal structure than those produced in Example I.

Upon thermal treatment the resulting carbon filaments contain in excess of 96 percent carbon by weight, and exhibit a specific gravity of about 1.65, a

denier per filament of about 0.7, an average single filament tensile strength of 13.8 grams per denier, an average single filament Young's modulus of 1700 grams per denier, and an elongation of 0.78 percent.

For comparative purposes Examples I and II are repeated with the exception that the N,N-dimethylformamide containing as-spun acrylonitrile homopolymer filaments are collected on a bobbin, and are next drawn to approximately the same total draw ratio while in contact with a hot shoe having a length of about 2 feet in the absence of prior contact with a water bath.

More specifically, the N,N-dimethylformamide containing filaments are fed to a hot shoe maintained at 165°C. at an input speed of 20 meters/minute and are withdrawn from the same at a rate of 132 meters/minute. The filaments are drawn at a draw ratio of 6.6:1.

See FIG. 2, and FIG. 4 of our U.S. Ser. No. 265,384, filed June 22, 1972, entitled "Improved Acrylic Filaments Which Are Particularly Suited for Thermal Conversion to Carbon Filaments" which illustrate the resulting acrylic filaments when examined under a scanning electron microscope and under a dark field optical microscope. The filaments possess a dogbone shaped cross-sectional configuration, a denier per filament of 1.47, an average single filament tensile strength of 3.6 grams per denier, an average single filament initial modulus of 77 grams per denier, an elongation of 12 percent, and a crystalline orientation by wide angle X-ray analysis of 14 degrees. The filaments lack the highly microporous and fibrillar internal structure exhibited by the filaments of Examples I and II. More specifically, the conventionally hot shoe drawn filaments of the comparative example exhibit an equatorial small angle X-ray scattering intensity of only 6.4 counts per second at a $1/d$ value of $5 \times 10^{-3}A^{(-1)}$.

EXAMPLE III

A further embodiment of the process of the present invention is carried out wherein a commercially available dry spun acrylonitrile copolymer tow serves as the starting material. The acrylonitrile copolymer consists of about 94 mol percent acrylonitrile units, about 5.5 mol percent of methyl acrylate units, and about 0.5 mol percent of copolymerized sulfonate dye site units. The tow consists of about 40,000 continuous filaments and has a total denier of about 120,000.

The acrylonitrile copolymer tow was previously formed via dry spinning. The tow has been washed, drawn, dried, and relaxed prior to purchase to remove the spinning solvent and possesses a microporous internal structure.

The tow is continuously passed for a residence time of about 7 seconds through a water bath maintained at 52°C. wherein the tow becomes water-laden and has excess water adhering to the surface of the same as it is withdrawn from the water bath. The tow is next passed around a plurality of heated rolls maintained at a surface temperature of 90°C. wherein excess water adhering to the surface thereof is substantially removed. The internal microporous structure of the filaments of the tow remains water-laden.

The water-laden tow is next passed at a rate of 10 meters/minute from the heated rolls to a drawing zone which is provided with saturated steam at about 100°C. The tow is axially suspended within the drawing zone during drawing. Tensioning rolls are positioned outside each end of the drawing zone containing the saturated steam atmosphere and exert a longitudinal tension upon the tow while passing through the drawing zone. The filaments of the tow are drawn at a draw ratio of 2:1. The drawn tow is taken up on a bobbin at a rate of 20 meters/minute, and is dried.

These filaments possess a denier per filament of 1.43, an average single filament tensile strength of 4.75 grams per denier, an average single filament initial modulus of 138 grams per denier, an elongation of 9.5 percent, and a crystalline orientation by wide angle X-ray analysis of 16 degrees. More importantly, these filaments exhibit a highly microporous and fibrillar internal structure as evidenced by an equatorial small angle X-ray scattering intensity of 93 counts per second at a $1/d$ value of $5 \times 10^{-3}A^{(-1)}$, and are particularly suited for thermal conversion to carbon filaments.

For comparative purposes the process of Example III is repeated with the exception that the commercial acrylonitrile copolymer tow is not passed through the water bath and over the plurality of heated rolls prior to drawing in steam. More specifically, the dry tow is passed at a rate of 10 meters per minute to the drawing zone which is provided with saturated steam at 100°C. The filaments of the tow are drawn at a draw ratio of 2:1. The drawn tow is taken up on a bobbin at a rate of 20 meters/minute.

The filaments resulting from this comparative drawing procedure possess a denier per filament of 1.55, an average single filament tensile strength of 4.49 grams per denier, an average single filament initial modulus of 120 grams per denier, an elongation of 9.69 percent, and a crystalline orientation by wide angle X-ray analysis of 14 degrees. However, these filaments exhibit an equatorial small angle X-ray scattering intensity of only 32 counts per second at a $1/d$ value of $5 \times 10^{-3}A^{(-1)}$, and accordingly lack the desired microporous and fibrillar internal structure which is particularly desirable in an acrylic filament intended for use as a precursor in the formation of a carbon filament.

Although the process of the present invention has been described with preferred embodiments, it is to be understood that variations and modifications may be employed in the acrylic filament formation technique without departing from the concept of the present invention.

We claim:

1. In a process for the production of a carbon filament from a dry spun acrylic filament selected from the group consisting essentially of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent acrylonitrile units and up to about 15 mol percent of one or more copolymerized monovinyl units which is capable of absorbing water, comprising thermally stabilizing said filament until non-burning when subjected to an ordinary match flame, and heating said stabilized filament in a non-oxidizing atmosphere at a temperature of at least about 1000°C. until a carbonaceous filament is formed which contains at least about 90 percent carbon by weight; the improvement comprising contacting said dry spun acrylic filament prior to said thermal stabilization with water at a temperature of about 20° to 90°C. until said filament substantially becomes water-laden, and drawing the resulting water-laden acrylic filament while suspended in a heated gaseous atmosphere at a temperature of at least 100°C. to form an acrylic filament having a highly microporous and fibrillar internal structure which is particularly suited for thermal conversion to a carbon filament.

2. An improved process according to claim 1 wherein said acrylic filament is an acrylonitrile homopolymer.

3. An improved process according to claim 1 wherein said water is provided at a temperature of about 40° to 60°C. when contacted with said dry spun acrylic filament.

4. An improved process according to claim 1 wherein said drawing of said water-laden filament is conducted in a heated gaseous atmosphere at a temperature of about 100° to 180°C.

5. An improved process according to claim 4 wherein said heated gaseous atmosphere is saturated steam.

6. In a process for the production of a carbon filament from a dry spun acrylic filament selected from the group consisting essentially of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent acrylonitrile units and up to about 15 mol percent of one or more copolymerized monovinyl units which is capable of absorbing water, comprising thermally stabilizing said filament until non-burning when subjected to an ordinary match flame, and heating said stabilized filament in an inert atmosphere at a temperature of at least about 1000°C. until a carbonaceous filament is formed which contains at least about 90 percent carbon by weight; the improvement comprising contacting said dry spun acrylic filament containing 5 to 30 percent by weight of water-miscible solvent prior to said thermal stabilization with water at a temperature of about 20° to 90°C. until residual solvent present therein is substantially removed and water is provided within micropores present therein, and drawing the resulting water-laden acrylic filament while suspended in a heated gaseous atmosphere at a temperature of at least 100° C. wherein the micropores present therein are substantially elongated and an acrylic filament is formed having a highly microporous and fibrillar internal structure which is particularly suited for thermal conversion to a carbon filament.

7. An improved process according to claim 6 wherein said acrylic filament is an acrylonitrile homopolymer.

8. An improved process according to claim 6 wherein said water-miscible solvent is selected from the group consisting essentially of N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, and N-methyl-2-pyrrolidone.

9. An improved process according to claim 6 wherein said drawing of said water-laden acrylic filament is conducted in a heated gaseous atmosphere at a temperature of about 100° to 180°C.

10. An improved process according to claim 9 wherein said heated gaseous atmosphere is saturated steam.

11. In a process for the production of a carbon filament from a dry spun acrylic filament selected from the group consisting essentially of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent acrylonitrile units and up to about 15 mol percent of one or more copolymerized monovinyl units which is capable of absorbing water, comprising thermally stabilizing said filament until nonburning when subjected to an ordinary match flame, and heating said stabilized filament in an inert atmosphere at a temperature of at least about 1000°C. until a carbonaceous filament is formed which contains at least about 90 percent carbon by weight; the improvement comprising:

a. providing a spinning solution having a low shear viscosity of about 100 to 1000 poise measured at 100°C. comprising (1) said acrylic polymer in a concentration of about 20 to 30 percent by weight based upon the total weight of the solution, and (2) a solvent selected from the group consisting of N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, and N-methyl-2-pyrrolidone,

b. extruding said solution of said acrylic polymer into a spinning zone containing an evaporative atmosphere to form a dry spun acrylic filament containing about 5 to 30 percent solvent by weight,

c. continuously passing said dry spun acrylic filament from said spinning zone to a first drawing zone containing a saturated steam atmosphere provided at about 100° to 120°C.,

d. drawing said dry spun acrylic filament containing about 5 to 30 percent solvent by weight at a draw ratio of about 1.5:1 to 6:1 while passing through said first drawing zone to form an acrylic filament containing a microporous internal structure,

e. contacting said resulting acrylic filament containing a microporous internal structure with water maintained at about 20° to 90°C. wherein the residual solvent present therein is substantially removed and replaced by water, and

f. drawing the resulting water-laden acrylic filament containing a microporous internal structure at a draw ratio of about 2:1 to 8:1 while passing through a second drawing zone containing steam provided at about 100° to 180°C. wherein the micropores present therein are substantially elongated to form an acrylic filament having a highly microporous and fibrillar internal structure which is particularly suited for thermal conversion to a carbon filament.

12. An improved process according to claim 11 wherein said acrylic filament is an acrylonitrile homopolymer.

13. An improved process according to claim 11 wherein said solvent is N,N-dimethylformamide.

14. An improved process according to claim 11 wherein said spinning solution contains said acrylic polymer in a concentration of about 24 to 27 percent by weight based upon the total weight of the solution.

15. An improved process according to claim 11 wherein said first drawing zone and said second drawing zone contain saturated steam having a temperature of about 100°C.

16. In a process for the production of a carbon filament from a dry spun acrylic filament selected from the group consisting essentially of an acrylonitrile homopolymer and an acrylonitrile copolymer which contains at least about 85 mol percent acrylonitrile units and up to about 15 mol percent of one or more copolymerized monovinyl units which is capable of absorbing water, comprising thermally stabilizing said filament until non-burning when subjected to an ordinary match flame, and heating said stabilized filament in an inert atmosphere at a temperature of at least about 1000°C. until a carbonaceous filament is formed which contains at least about 90 percent carbon by weight; the improvement comprising:

a. providing a spinning solution having a low shear viscosity of about 200 to 500 poise measured at 100°C. comprising (1) said acrylic polymer in a concentration of about 24 to 27 percent by weight based upon the total weight of the solution, and (2) a N,N-dimethylformamide solvent,

b. extruding said solution of said acrylic polymer into a spinning zone containing an evaporative atmo-

sphere to form a continuous length of dry spun acrylic filament containing about 5 to 30 percent N,N-dimethylformamide by weight,

c. continuously passing said dry spun acrylic filament from said spinning zone to a first drawing zone containing a saturated steam atmosphere provided at about 100°C.,

d. drawing said dry spun acrylic filament containing about 5 to 30 percent N,N-dimethylformamide by weight at a draw ratio of about 2:1 to 3.5:1 while passing through a first drawing zone to form an acrylic filament containing a microporous internal structure, e. contacting said resulting continuous length of acrylic filament containing a microporous internal structure with water maintained at about 40° to 60°C. wherein the residual N,N-dimethylformamide present therein is substantially removed and replaced by water, and

f. drawing the resulting water-laden acrylic filament containing a microporous internal structure at a draw ratio of about 2:1 to 3:1 while passing through a second drawing zone containing saturated steam provided at about 100°C. wherein the micropores present therein are substantially elongated to form an acrylic filament having a highly microporous and fibrillar internal structure which is particularly suited for thermal conversion to a carbon filament.

17. An improved process according to claim **16** wherein said acrylic filament is an acrylonitrile homopolymer.

18. An improved process according to claim **16** wherein said spinning solution contains said acrylic polymer in a concentration of about 25 percent by weight based upon the total weight of the solution.

19. An improved process according to claim **16** wherein said evaporative atmosphere into which said solution is extruded is nitrogen.

20. An improved process according to claim **16** wherein said dry spun acrylic filament when initially introduced into said first drawing zone contains N,N-dimethylformamide in a concentration of about 8 to 10 percent by weight.

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