ABSTRACT

An improved carbon filament is provided having an internal structure capable of increasing the amount of work required to break the filament. The internal structure of the carbon filaments of the present invention as evidenced by the means apparent fracture surface energy of the same facilitates the enhancement of satisfactory strength properties even if accompanied by the presence of gross inhomogeneities and structural flaws such as commonly encountered in carbon filaments of the prior art.

10 Claims, 4 Drawing Figures
Fig. 3

Mean single filament tensile strength (kpsi) vs. mean apparent fracture surface energy (Joules/square meter).

- Average flaw size, C
  - 0.3 \( \mu \)
  - 0.5 \( \mu \)
  - 1.0 \( \mu \)
  - 1.5 \( \mu \)
CARBON FILAMENTS CAPABLE OF SUBSTANTIAL CRACK DIVERSION DURING FRACTURE

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of our U.S. Ser. No. 28,545, filed Apr. 14, 1970 entitled “Improved Process for the Production of Acrylic Filaments” (now U.S. Pat. No. 3,657,409).

BACKGROUND OF THE INVENTION

Carbon filaments have long been known and are discussed in the technical literature. 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. R. Land 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 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 John W. Johnson appearing in Applied Polymer Symposium, Vol. 9, Pages 229-243 (1969), entitled “Factors Affecting the Tensile Strength of Carbon-Graphite Fibres.”

The present invention provides a novel approach to the improvement of carbon filaments. The carbon filaments of the present invention possess an internal structure unlike that exhibited by the carbon filaments of the prior art as discussed in detail hereafter.

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

It is an object of the invention to provide carbon filaments possessing an improved internal structure.

It is an object of the invention to provide carbon filaments capable of substantial crack diversion upon fracture.

SUMMARY OF THE INVENTION

An improved carbon filament is provided comprising at least 90 percent carbon by weight having an unusually highly developed microporous and fibrillar internal structure substantially coextensive with the length of the filament capable of diverting a propagating crack during fracture thereby increasing the amount of work required to break the filament as evidenced by a mean apparent fracture surface energy of at least 50 joules per square meter.

In a preferred embodiment of the invention the carbon filaments contain at least 95 percent carbon by weight and additionally exhibit a mean single filament Young's modulus of about 20 to 50 million psi.

DESCRIPTION OF DRAWINGS

FIG. 1 and FIG. 2 are photographs made with the aid of a scanning electron microscope at a magnification of 5,740X of matching sides of the primary fracture surface of a carbon filament of the present invention formed in accordance with the procedure described in the Example which shows a flaw having a maximum dimension of 1.4 micron.

FIG. 3 is a graph which illustrates for carbon filaments of 35 million psi Young's modulus having various average flaw sizes the relationship between the mean apparent fracture surface energy and the mean single filament tensile strength.

FIG. 4 is a schematic view of a representative apparatus arrangement suitable for forming acrylic filaments which are subsequently thermally transformed into the carbon filaments of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The improved carbon filaments of the present invention are derived from polymeric fibrous materials. For instance, an acrylic polymer may be formed into an acrylic filament possessing a requisite internal structure, and the resulting acrylic filament converted to a carbon filament possessing an improved internal structure through appropriate thermal processing.

Acrylic filament precursors suitable for thermal conversion into the improved carbon filaments of the present invention may be formed in accordance with embodiments of the process described in our commonly assigned U.S. Ser. No. 28,545, filed Apr. 14, 1970, and entitled “Improved Process for the Production of Acrylic Filaments” (now U.S. Pat. No. 3,657,409) which is herein incorporated by reference. Such improved acrylic filaments are claimed in our commonly assigned U.S. Ser. No. 244,541, filed concurrently herewith, entitled “Improved Acrylic Filaments Which
3,841,079

Are Particularly Suited for Thermal Conversion to Carbon Filaments."

More specifically, the fiber-forming acrylic polymer selected for use in the formation of the acrylic precursor may be 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 graftification Catalysts may optionally be incorporated in the bulk acrylic polymer prior to spinning.

The solvent utilized to form the spinning solution may be dimethylacetamide. The solvent is sometimes identified as N,N-dimethylacetamide or DMAC, and the chemical formula CH₃CON(CH₃)₂. The standard technical or commercial grade of dimethylacetamide may be employed as the solvent in the formation of the spinning solution.

The spinning solution may be prepared by dissolving sufficient acrylic polymer in the dimethylacetamide solvent to yield a solution suitable for extrusion containing from about 15 to 30 percent acrylic polymer by weight based upon the total weight of the solution, and preferably from about 18 to 25 percent by weight. In a particularly preferred embodiment of the invention the spinning solution contains the acrylic polymer in a concentration of about 20 to 22 percent by weight based upon the total weight of the solution. The low shear viscosity of the spinning solution should be within the range of about 80 to 3,000 poise measured at 25°C, and preferably within the range of about 125 to 1,500 poise measured at 25°C. If the spinning solution low shear viscosity is much below about 80 poise measured at 25°C, spinning breakdowns commonly occur. If the spinning solution low shear viscosity is much above about 3,000 poise measured at 25°C, extremely high spinning pressures are required and plugging of the extrusion orifice may occur.

In a preferred precursor formation technique 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 solution should also be fluidly and mobile fluidly and be 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 dimethylacetamide solvent commonly exhibits a relatively constant low shear viscosity of about 150 poise measured at 25°C following 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 dimethylacetamide) tends to increase in viscosity upon standing and exhibits a low shear viscosity of about 1,000 poise measured at 25°C after about 2 ½ hours. The lithium chloride may be dissolved in the dimethylacetamide solvent either simultaneously with the acrylic polymer or before or after the acrylic polymer is dissolved therein. Minor quantities of preoxidation or graftification 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 wet 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 dissolved therein is extruded into a coagulation bath under conditions capable of forming an acrylic filament having an internal structure which is capable upon subsequent thermal treatment of yielding the improved carbon filaments of the present invention.

It has been found that acrylic filaments possessing the requisite internal structure are produced when an essentially non-aqueous coagulation bath is utilized having a temperature of about 0° to 45°C. (preferably about 10° to 35°C) which consists essentially of about 55 to 85 percent by weight of ethylene glycol and about 15 to 45 percent by weight of dimethylacetamide. When employing dimethylacetamide in the coagulation bath in concentrations much greater than about 45 percent by weight, then filament breakage tends to occur at the spinneret. When employing dimethylacetamide in the coagulation bath in concentrations much less than about 15 percent by weight, then the resulting filaments tend to lose their substantially round cross-section and have a tendency to exhibit a more pronounced bean-shaped configuration. In a preferred embodiment of the invention the coagulation bath consists essentially of about 60 to 75 percent by weight of ethylene glycol and about 25 to 40 percent by weight of dimethylacetamide. In a particularly preferred embodiment of the invention the coagulation bath consists essentially of about 60 percent by weight of ethylene glycol and about 40 percent by weight of dimethylacetamide. At the relatively low coagulation bath temperatures employed the coagulation rate tends to be relatively slow and to enhance the formation of the desired fiber internal structure.

The temperature of the spinning solution at the time of its extrusion should be within the range of about 10°C. to about 90°C., and preferably at about 20° to 30°C. In a particularly preferred embodiment of the invention the spinning solution is provided at room temperature, e.g., about 25°C., which thereby facilitates expeditious handling and storage of the same.

The spinneret utilized during the extrusion 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, taws of up to 20,000, or more, continuous filaments may be formed. The spinneret preferably contains holes having a diameter between about 50 to 150 microns when producing relatively low denier filaments having an as-spun denier of about 8 to 24 denier per filament, and
holes of about 300 to 500 microns when producing relatively high denier filaments having as-spun denier of about 100 to 1,500 denier per filament. Extrusion pressures between about 100 and 700 psig may be conveniently selected, and preferably between about 100 and 400 psig. Spinning or extrusion speeds of about 0.5 to 10 meters per minute (e.g., 3 to 6 meters per minute) may be employed.

Throughout the extrusion process the coagulation bath is preferably circulated. A relatively constant composition within the coagulation bath may be maintained through the continuous withdrawal and purification of the same. Alternatively, additional dimethylacetamide may be continuously added to the coagulation bath to preserve the desired proportion of dimethylacetamide to ethylene glycol within the same. The length of the coagulation bath is adjusted so that the resulting as-spun filaments are present within the coagulation bath for a residence time of at least about 6 seconds. For instance, residence times of about 6 to 300 seconds may be conveniently selected. Residence times less than about 6 seconds tend to result in an insufficiently developed fibrillar structure within the as-spun filaments. Residence times for the as-spun filaments in the coagulation bath in excess of 300 seconds tend to yield no commensurate advantage. Particularly preferred residence times for the as-spun filament in the coagulation bath range from about 6 to 50 seconds.

The resulting as-spun filament is next washed with water to remove dimethylacetamide solvent from the same. The as-spun filament is preferably washed with water until substantially all residual amounts of solvent, coagulants, bath and, inorganic compounds (e.g., lithium chloride), if any, are removed from the same. It is essential that the filament first be exposed to a relatively cool water wash medium at a temperature of about 10°C to 50°C, and preferably at about 10°C to 30°C, and most preferably at room temperature (e.g., about 25°C), for at least about 25 seconds. The entire wash treatment may be conducted at a temperature within the range of about 10°C to 50°C. Alternatively the washing of the filament may be subsequently continued at a more highly elevated temperature, e.g., in excess of about 30°C, to remove additional solvents. In a preferred embodiment of the invention the initial cool water wash is conducted for at least about 50 seconds.

When the entire wash is conducted at a relatively cool wash temperature of about 10°C to 50°C, wash times of about 25 to 240 seconds and preferably about 50 to 120 seconds are commonly utilized depending upon the filament denier. Longer wash times tend to yield no commensurate advantage.

It has been found that if the initial cool water wash described above is essential in order to preserve the requisite fiber homogeneity in the acrylic filament precursor. The cooling wash is conducted at a temperature substantially higher than about 50°C when the resulting washed filament tends to contain a significant number of macrovoids and tends to flatten. At temperatures below about 10°C, the washing procedure tends to be unduly slow. The residual dimethylacetamide content of the washed acrylic filaments preferably is no more than about 5 percent dimethylacetamide by weight, and most preferably no more than about 0.1 percent by weight, prior to subsequent processing.

The water wash treatment is conveniently conducted in an in-line operation with the filament after it leaves the coagulation bath being continuously passed through a water wash medium which is continuously regenerated. Conventional filament wash rolls may be utilized. The filament alternatively may be washed with water while wound upon a perforated bobbin, or by the use of other washing means as will be apparent to those skilled in the art.

The as-spun and washed acrylic filament is drawn or stretched from about 1.5 times its original length up to the point at which the filament breaks to orient the same and to thereby enhance its tensile properties. Total draw ratios above about 1.5:1 to 15:1 may commonly be selected. The drawing is commonly conducted at an elevated temperature and preferably at a total draw ratio of between about 3:1 and 12:1. The dense internal filament structure makes possible the use of relatively high total draw ratios indicated. As will be apparent to those skilled in the art, the drawing of the as-spun and washed acrylic filament may be conducted by a variety of techniques. For instance, it is possible for the drawing to be conducted while the filament is (a) immersed in a heated liquid draw medium, (b) suspended in a heated gaseous atmosphere, (e.g., at a temperature of about 120°C to 200°C) or (c) in contact with a heated solid surface (e.g., at a temperature of about 130°C to 170°C). If desired, the total draw imparted to the filament may be conducted by a combination of the foregoing techniques. When draw techniques (b) and (c) are utilized, it is essential that the acrylic filament be provided to the draw zone in an essentially dry form in order to avoid formation. When draw technique (a) is employed, the acrylic filament is subsequently washed to remove the draw medium and is dried. Additionally, the liquid draw medium may also serve a washing and/or coagulating function wherein residual quantities of dimethylacetamide are removed from the water washed fiber.

In a preferred embodiment of the invention the initial cool water wash is conducted for at least about 30 seconds.
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 peroxidized 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. Preferred stabilization procedures are described in commonly assigned U.S. Ser. No. 749,957, filed Aug. 5, 1968 (now abandoned), of Dagobert E. Stuetz, and in U.S. Pat. No. 3,539,295, of Michael J. Ram, which are herein incorporated by reference. Other stabilization procedures capable of imparting thermal stability to the acrylic filaments may be selected. The highly fibrillar internal structure required to make possible the formation of the claimed carbon filaments is retained throughout the stabilization reaction.

The stabilized acrylic filaments are converted to the carbon filaments of the present invention by thermal treatment at a more highly elevated temperature of at least 1,000°C, e.g., 1,000°C to 2,000°C, 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 by 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. Carbon filaments of optimum tensile strength are formed when the maximum temperature provided in the heating zone is about 1,500°C to 1,900°C. (e.g., 1,800°C). The carbon fibers are preferably formed on a continuous basis by continuous passage through a heating zone containing a non-oxidizing atmosphere and a temperature gradient in which the stabilized acrylic filaments are gradually raised to the maximum carbonization temperature. During the thermal treatment at 1,000°C to 2,000°C, a highly developed microporous structure is inherently imparted to the resulting carbon filaments wherein a large number of elongated micropores of up to about 25 Angstroms (e.g., about 5 to 15 Angstroms) in thickness are disposed between the highly fibrillar internal structure which are largely preserved during the thermal treatment. The increased presence of the micropores within the highly fibrillar internal structure is confirmed by small angle X-ray analysis.

The carbon filaments of the present invention commonly exhibit a mean single-filament Young's modulus of about 20 to 50 million psi. As discussed elsewhere, the internal structure of the carbon filaments of the present invention provides carbon filaments of improved tenacity in spite of structural flaws such as those commonly encountered in the prior art. For instance, carbon filaments commonly possess flaws of 0.5 micron and larger as discussed in the Johnson, and Thorne and Johnson articles cited earlier.

The improved carbon fibers of the present invention have an unusually highly developed microporous and fibrillar internal structure which is capable of diverting a propagating crack during fracture thereby increasing the amount of work required to break the filament as evidenced by a mean apparent fracture surface energy (i.e., $\gamma_{av}$) of at least 50 joules per square meter (e.g., 50 to 150, or more, joules per square meter). In a preferred embodiment the carbon filaments exhibit a mean apparent fracture surface energy of at least 60 joules per square meter. In a particularly preferred embodiment the carbon filaments exhibit a mean apparent fracture surface energy of at least 70 joules per square meter.

It has been found that carbon/graphite filaments fail in a brittle fashion and that the Griffith failure criterion can be utilized to elucidate the fracture phenomenology. One form of the simple Griffith equation which has been applied to the fracture of many brittle materials is as follows:

$$WTB = \frac{1}{2} t_0 e_b = \frac{t_0^2}{2E} = \gamma_{av} \pi C$$

where

$$WTB = \text{work-to-break (energy to fracture)}.$$

$t_0$ = breaking stress

$e_b$ = breaking strain

$E = \text{Young's modulus}$

$\gamma_{av} = \text{apparent fracture surface energy}$

$C = \text{size of critical flaw at which fracture initiated}$

$\pi = 3.14 \ldots$

For an ideally brittle material, $\gamma_{av}$ should correspond to the energy required to break primary chemical bonds. It is recognized, however, that in all but extremely rare cases of apparently brittle fracture, large amounts of plastic work are done at the crack tip, leading to observed values of $\gamma_{av}$ much higher than would be expected from bond-breaking alone. See, for example, "Fracture" edited by H. Liebowitz, Academic Press, New York (1968). The apparent fracture surface energy, $\gamma_{av}$, is an intrinsic property of the carbon fiber and accordingly is dependent upon the internal physical structure of the carbon fiber.

A technique for the determination of the mean apparent fracture surface energy, $\gamma_{av}$ for a given carbon filament is described in detail below. Generally stated the $WTB$ and $C$ for a given carbon filament are determined and the mean apparent fracture surface energy is calculated therefrom.

1. Single carbon filaments individually are broken while immersed in glycerin and the stress, strain, and Young's modulus determined by conventional fiber testing techniques. The use of a glycerin bath minimizes the formation of secondary fracture surfaces which tend to be formed in an open atmosphere.

2. The resulting pair of ends for each broken filament is examined in the field of a scanning electron microscope and compared to assure a match thus inuring that a primary fracture surface is being examined. See, for instance, FIG. 1 and FIG. 2 which are photographs made with the aid of a scanning electron microscope of the primary fracture surface of a carbon filament of the present invention formed in accordance with the procedure described in the Example.

3. The critical flaw, $C$, which initiated the fracture is located and the longest dimension on the primary fracture surface is measured. In FIG. 1 and FIG. 2...
the largest dimension of the flaw on the primary fracture surface of each broken end was found to be 1.4 micron.

The above procedure is repeated a number of times for a given sample of carbon filaments and the values obtained for WTB and C are plotted as log WTB vs. log C. A least squares line is drawn through the points assuming a slope of −1 in accordance with the theoretical prediction of the Griffith equation. The intercept of this line is accordingly log (γ/π) from which the mean γ, or mean apparent fracture surface energy, is determined. It is recommended that at least four carbon filaments be broken as described above when determining the mean apparent fracture surface energy for a given sample of carbon filaments. The results obtained are, of course, more statistically accurate as the number of breaks increases.

The mean apparent fracture surface energies of a wide variety of carbon filaments have been determined. In all instances, the mean apparent fracture surface energies were substantially below that of the carbon filaments of the present invention. The following Table I sets forth the average flaw size and mean apparent fracture surface energy obtained for representative carbon filaments.

<table>
<thead>
<tr>
<th>Carbon Fiber Source</th>
<th>Carbon Fiber Designation</th>
<th>Average Single Filament Young's Modulus M psi</th>
<th>Average Flaw Size micron</th>
<th>Mean Apparent Fracture Surface Energy joules/sq.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Lakes Carbon Corp.</td>
<td>3T¹</td>
<td>31</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>4T²</td>
<td>39</td>
<td>0.8</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>5T²</td>
<td>48</td>
<td>0.9</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>6T²</td>
<td>60</td>
<td>0.9</td>
<td>26</td>
</tr>
<tr>
<td>Hercules, Inc.</td>
<td>HT-S²</td>
<td>39</td>
<td>0.7</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>A-S³</td>
<td>36</td>
<td>1.1</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>HM-S⁴</td>
<td>64</td>
<td>1.4</td>
<td>25</td>
</tr>
<tr>
<td>Johnson &amp; Thorne Acrilan Carbon Fibers⁵</td>
<td>20</td>
<td>0.7</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Celanese</td>
<td>A⁶</td>
<td>35</td>
<td>1.3</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>B⁶</td>
<td>35</td>
<td>1.3</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>C⁶</td>
<td>35</td>
<td>1.3</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>D⁶</td>
<td>37</td>
<td>1.4</td>
<td>14</td>
</tr>
</tbody>
</table>

1 Derived from a dry spun Orion acrylic precursor.
2 Derived from a wet spun Courtaulds acrylic precursor (salolin thioacetate spinning solution).
3 Shown in FIG. 5, following Page 661, of Vol. 2, of Carbon, article by J. W. Johnson and D. J. Thorne, cited earlier (wet spun from DMAC spinning solution employing an aqueous coagulation bath).
4 Derived from various dry spun acrylic precursors.

An unusually high mean apparent fracture surface energy enables a larger average flaw size to be tolerated while still obtaining a high strength carbon filament. As fracture is initiated and a propagating crack meets a microvoid between fibrils, the crack is diverted and additional energy is consumed. For example, see the following Table II.

<table>
<thead>
<tr>
<th>Mean Apparent Fracture Surface Energy joules/sq.m.</th>
<th>Average Flaw Size micron</th>
<th>Average WTB psi</th>
<th>Average 6b ksi</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.5</td>
<td>1260</td>
<td>304</td>
</tr>
<tr>
<td>27</td>
<td>0.5</td>
<td>2540</td>
<td>434</td>
</tr>
<tr>
<td>65</td>
<td>0.5</td>
<td>5850</td>
<td>650</td>
</tr>
<tr>
<td>65</td>
<td>1.2</td>
<td>2540</td>
<td>434</td>
</tr>
</tbody>
</table>

| FIG. 3 illustrates for carbon filaments of 35 million psi Young's modulus having various average flaw sizes the relationship between the mean apparent fracture surface energy and the mean single filament tensile strength. | ethylene glycol and 40 parts by weight dimethylacetamide and is provided at a temperature of 36°C. The coagulation bath is caused to flow concurrently with coagulated filament 8 and is maintained at a relatively constant composition by the continuous addition of |
3,841,079

ethyleneglycol to the same and the continuous withdrawal of a portion of the bath. The coagulation bath has a length of 37 inches and the coagulated filaments are maintained in the same for a residence time of about 9 seconds.

The coagulated filaments pass under guide 10 which is immersed in coagulation bath 6 and are conveyed to a skewed roll 12 and wash roll 14 which is partially immersed in water bath 16 which is maintained at 23°C. The coagulated filaments are taken up on roll 12 at a rate of 6 meters per minute. The filaments are wrapped about skewed roll 12 and wash roll 14 for a residence time of about 125 seconds during which time the filaments are immersed in water for approximately 25 seconds and withdrawn with water adhering to the same during which time substantially all residual amounts of dimethylacetamide are removed from the same.

The washed filaments are next continuously passed through stretch bath 17 having a length of 15 inches which is provided with glycerin at 80°C. Rollers 18 and 20 situated outside the stretch bath and rollers 22 and 24 immersed within the stretch bath guide the filaments during the stretching operation. The filaments are next taken up on skewed roll 26 and wash roll 28 which is partially immersed in a water wash bath 30 provided at 22°C which is substantially identical to that of wash bath 16. The filaments are taken up on skewed roll 26 at a rate of 12 meters per minute and are accordingly drawn at a draw ratio of 2:1 while immersed in the glycerin stretch bath. The filaments are immersed in the water wash bath 30 for approximately 12.5 seconds during which time residual quantities of glycerin are substantially removed from the same. The water present in wash bath 30 is circulated and is constantly regenerated. The washed filaments are next passed to skewed roll 32 and drying roll 34 where residual quantities of moisture are expelled from the same. Drying roll 34 is steam heated and maintained at a constant temperature of approximately 95°C.

The washed and dried filaments are next passed over a 2-foot heated draw shoe which is provided at a constant temperature of 145°C. The residence time of the filaments while in contact with the hot shoe 36 is 1.25 second. The drawn filaments are collected on takeup roll 38 at a rate of 60 meters per minute.

Two of the drawn filament bundles are next plied to form a continuous length of acrylic fibrous material consisting of 800 continuous filaments. This resulting continuous length is next subjected to a brief thermal pretreatment in accordance with the teachings of commonly assigned U.S. Ser. No. 17,962, filed Mar. 9, 1970 (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 is next passed for about 180 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 of about 10.1 percent by weight when subjected to the Unterzaucher analysis.

The continuous length of stabilized filaments is next converted to the improved carbon filament of the present invention 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 grams 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 1,500°C. in about 200 seconds where it was maintained at 1,500°C. ± 25°C. for about 48 seconds.

The resulting carbon filaments contain in excess of 98 percent carbon by weight, and are found to possess a mean apparent fracture surface energy of 82 joules per square meter. The mean apparent fracture surface energy was calculated as heretofore described.

FIG. 1 and FIG. 2 are photographs made with the aid of a scanning electron microscope at a magnification of 5,740X of matching sides of the primary fracture surface of a representative carbon filament which shows a flaw having a maximum dimension of 1.4 micron. The average flaw size for the carbon filaments produced is found to be 2.7 microns.

The resulting carbon filaments additionally exhibit a specific gravity per filament of about 1.75, a denier per filament of 0.78, a mean single filament tensile strength of 350,000 psi, a mean single filament Young's modulus of 44 million psi, and an elongation of 0.78 percent.

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

We claim:

1. An improved carbon filament comprising at least 90 percent carbon by weight having an unusually highly developed microporous and fibrillar internal structure substantially coextensive with the length of said filament capable of diverting a propagating crack during fracture thereby increasing the amount of work required to break the filament as evidenced by a mean apparent fracture surface energy of at least 50 joules per square meter.

2. An improved carbon filament according to claim 1 wherein said filament is present in a multifilament yarn.

3. An improved carbon filament according to claim 1 wherein said filament is present in a multifilament tow.
4. An improved carbon filament according to claim 1 wherein said filament comprises at least 95 percent carbon by weight.
5. An improved carbon filament according to claim 1 wherein said filament comprises at least 98 percent carbon by weight.
6. An improved carbon filament according to claim 1 which exhibits a mean single filament Young's modulus of about 20 to 50 million psi.
7. An improved carbon filament according to claim 1 wherein the cross-sectional configuration thereof is substantially round.
8. An improved carbon filament according to claim 1 which exhibits a mean apparent fracture surface energy of at least 60 joules per square meter.

9. An improved carbon filament according to claim 1 which exhibits a mean apparent fracture surface energy of at least 70 joules per square meter.
10. An improved carbon filament comprising at least 95 percent carbon by weight which exhibits a mean single filament Young's modulus of about 20 to 50 million psi and has an unusually highly developed microporous and fibrillar internal structure substantially coextensive with the length of said filament capable of diverting a propagating crack during fracture thereby increasing the amount of work required to break the filament as evidenced by a mean apparent fracture surface energy of at least 70 joules per square meter.