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(54) HIGH STRENGTH POLYETHYLENE FIBER

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(57) **ABSTRACT**

A polyethylene fiber having high strength, which was not easily obtained by methods such as the conventional gel spinning method, includes crystals derived from a monoclinic crystal having a size of 9 nm or more. The tensile strength of the fiber can be 30 cN/dtex or more. This high strength polyethylene fiber is produced by mixing an ultra-high molecular weight polyethylene with a mixed solvent of a good solvent for polyethylene and a poor solvent for polyethylene to form a polyethylene dope, extruding the dope through an orifice, cooling the extruded dope, and drawing it into a filament yarn.

HIGH STRENGTH POLYETHYLENE FIBER

REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from Japanese Patent Application No. 2006-106306, filed Apr. 7, 2006, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a novel high strength polyethylene fiber which can be widely used for industrial applications, for example, high performance textiles such as various sport wears, bulletproof/protective wears and protective gloves, and various safety goods; various rope products such as tag ropes, mooring ropes, yacht ropes, and building ropes; various braid products such as fishing lines and blind cables; net products such as fishing nets and ball-protecting nets; reinforcing materials for chemical filters and battery separators; various nonwoven fabrics; curtain materials such as tents; reinforcing fibers for sport goods such as helmets and ski boards; and reinforcing fibers for composite products such as speaker cones, concrete reinforcing, and prepregs.

[0004] 2. Description of the Related Art

[0005] With regard to a high strength polyethylene fiber, it is known that a fiber having high strength and high elastic modulus, which has never been attained in the prior art, is obtained by a so-called "gel spinning method" using an ultrahigh molecular weight polyethylene as a raw material, and such a fiber having high strength and high elastic modulus has already been used widely for industrial applications (see, for example, Japanese Examined Patent Publication (Kokoku) No. 60-47922 and Japanese Examined Patent Publication (Kokoku) No. 64-8732).

[0006] Recently, the high strength polyethylene fiber has widely used in various applications, in addition to the above applications and, furthermore, not only higher strength and higher elastic modulus, but also an improvement of the productivity may be strongly required. One of the conditions that are necessary for productivity improvement of a polyethylene fiber is excellent drawability. In the production of the polyethylene fiber, as the maximum value of a draw ratio increases, a thread breakage rate during drawing decreases and a drawing speed can be more increased.

SUMMARY OF THE INVENTION

[0007] The present inventors provide a polyethylene fiber which enables high productivity that was not be easily attained by a method such as a conventional gel spinning method. As a result of intensive study so as to satisfy higher strength, higher elastic modulus, and improved productivity due to increased drawability, the present inventors have found the followings: drawability of an ultrahigh molecular weight polyethylene fiber is improved by mixing a poor solvent for polyethylene such as higher alcohol in addition to a good solvent for polyethylene such as decalin at the time of preparing solution. Also, it has been found that the high strength polyethylene fiber obtained by such a method has a characteristic crystal structure. Namely, the crystal size of a monoclinic crystal is larger than that which is considered based on a conventional finding. As a conventional finding, a polyethylene multifilament having high strength and high knot strength obtained by suppressing the crystal size of the monoclinic crystal (Citation: Japanese Unexamined Patent Publication (Kokai) No. 2006-45752)

[0008] According to the present invention, a high strength polyethylene fiber is provided.

[0009] 1. A high strength polyethylene fiber, which is characterized in that the size of a crystal derived from a monoclinic crystal is 9 nm or more.

[0010] 2. The high strength polyethylene fiber described in the item 1, which preferably has a tensile strength of 30 cN/dtex or more.

[0011] 3. The high strength polyethylene fiber described in the item 1, which can be produced by mixing an ultrahigh molecular weight polyethylene having an intrinsic viscosity of 8 dL/g or more with a mixed solvent of a solvent (A) as a good solvent for polyethylene and a solvent (B) as a poor solvent for polyethylene in a mixing ratio of the solvent (A) to the solvent (B) within a range from 20:80 to 99:1 (weight ratio) to form a mixed dope having a polyethylene concentration of 0.5% by weight or more and less than 50% by weight, extruding the dope through an orifice, cooling the extruded dope, and drawing it into a filament yarn.

[0012] 4. The high strength polyethylene fiber described in the item 3, wherein a mixed solvent of the solvent (A) having a viscosity index of 0.6 or more and the solvent (B) having a viscosity index of 0.6 or less can be used.

[0013] 5. The high strength polyethylene fiber described in the item 1, which may contain 5 ppm or more of the solvent having a viscosity index for polyethylene of 0.6 or less.

[0014] The present invention made it possible to provide a high strength polyethylene fiber having remarkably improved productivity, which was not easily obtained by a conventional gel spinning method.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The present invention will now be described in detail. Novel methods are preferably employed to obtain a fiber of the present invention. The methods for producing a fiber of the present invention include, but are not limited to, the below-described recommended methods. A high molecular weight polyethylene that can be used as a raw material has an intrinsic viscosity [η] of 8 dL/g or more when measured at a measuring temperature of 135° C. using decalin as a measuring solvent, and preferably 10 dL/g or more. When the intrinsic viscosity is less than 8 dL/g, the desired high strength fiber having strength of more than 30 cN/dTex is not obtained.

[0016] The ultrahigh molecular weight polyethylene of the present invention is characterized in that its repeating unit substantially comprises ethylene, and may be a copolymer with a small amount of the other monomers, for example, α-olefin, acrylic acid and its derivative, methacrylic acid and its derivative, or vinylsilane and its derivative; or may be a blend of two or more copolymers selected from these copolymers, a blend of an ethylene homopolymer and one or more of these copolymers, or a blend of other homopolymers consisting of α-olefin and one or more of these copolymers. In the production of the fiber of the present invention, a copolymer with α-olefin such as propylene or butane-1 is preferably used because an incorporation of a long- or short-chain branch to some extent enables stable production of the yarn in spinning and drawing processes. However, the excessive increase in the monomer content

other than ethylene can be disincentive for the drawing. From the viewpoint of getting a high strength and high modulus fiber, therefore, the monomer content other than ethylene is preferably 0.2 mol % or less in monomer unit, more preferably 0.1 mol % or less. As a matter of course, homopolymer consisting of ethylene only may be used.

[0017] The important factor in a method for producing a high strength polyethylene fiber with high productivity of the present invention is the solvent species used so as to prepare a solution of polyethylene. As the solvent, decalin, tetralin and paraffin have hitherto been known, and these solvents were selected because of good solubility for polyethylene. In view of productivity, when these solvents are used, there were problems that the breakage of the yarn occurs frequently in the drawing process as one of the production processes of the polyethylene fiber and the drawing rate can not be increased because of insufficient drawability. It is known that, regarding the interaction between the solvent and polyethylene molecules, spreading of polyethylene molecules in the solution drastically varies depending on not only solubility, but also the kind of the solvent selected. Consequently, it is considered that, when the molecular weight of polyethylene and the concentration of polyethylene molecules are the same in the solution, the space to be occupied by one molecule in the solution decreases as the degree of spreading of polyethylene molecules decreases, resulting in less entanglement of polyethylene molecules. Namely, it is believed that entanglement of polyethylene molecules, which is considered to exert a large influence on drawability upon production, can be reduced by selecting the solvent so as to decrease spreading of polyethylene molecules in the solution. Regarding spreading of polyethylene molecules due to the kind of the solvent, for example, a basic theory has been established as described in "Experimental New Polymer (Shin-Kobunshi Jikkengaku)". A brief summary is as follows. When flexible macromolecules of polyethylene is dissolved in a good solvent having good solubility, if a pair of segments located at a long distance along the same molecule approach with each other, a repulsive force becomes superior to an attractive force in the interaction between the segments, and thus the molecules tend to turn into a more spread state. On the other hand, when flexible macromolecules are dissolved in a poor solvent having inferior solubility, affinity between molecules and the solvent is inferior and an attractive force becomes superior to a repulsive force in the interaction between a pair of segments, and thus the molecules attempt to turn into a more shrunk state as compared with the case of using a good solvent. Therefore, when the poor solvent is used, the degree of spreading of molecules in the solution decreases as compared with the case of using the good solvent. Consequently, it is considered that entanglement of molecules decreases when using the poor solvent and thus it becomes possible to improve drawability. It is well known that the degree of spreading of molecules in the solution exerts an influence on the amount of the intrinsic viscosity measured. As is apparent from enormous experimental data, molecular weight dependency of the degree of spreading of molecules conforms to the power-law [Formula 1] in the region where the molecular weight M is sufficiently high.

$$[\eta] \propto M^{\alpha} \qquad \text{[Formula 1]}$$

[0018] In the above formula, α denotes a viscosity index. As a result of intensive study, it becomes possible to remarkably improve drawability upon production by selecting the kind of the solvent whose viscosity index satisfies specific conditions. The specific conditions are as follows. That is, a mixed solvent shall contains 20% by weight or more and less than 99% by weight of a solvent (A) having a viscosity index of 0.6 or more and 1% by weight or more and less than 80% by weight of a solvent (B) having a viscosity index of 0.6 or less. It is not preferred to use a mixture solvent containing 99% by weight or more of the solvent (A) and less than 1% by weight of the solvent (B) because less effect is exerted on drawability. It is not preferred to use a mixture solvent containing 20% by weight or less of the solvent (A) and 80% by weight or more of the solvent (B) because solubility of polyethylene drastically deteriorates.

[0019] The solvent having a viscosity index of 0.6 or less can be selected from among polyethylene solvents described in "Polymer Handbook Fourth Edition", Chapter 4.

[0020] In the method of the present invention, the polyethylene concentration in the solution may vary depending on properties of a solvent and the molecular weight and molecular weight distribution of polyethylene. When using polyethylene having particularly high molecular weight, for example, an intrinsic viscosity of 14 dL/g or more when measured at a measuring temperature of 135° C. using decalin as a solvent in a mixed dope having a concentration of 50% by weight or more, brittleness breakage is likely to occur during spinning because of high viscosity, and thus it becomes very difficult to perform spinning. On the other hand, when using a mixed dope having a concentration of less than 0.5% by weight, there is such a drawback that the yield decreases, resulting in increased cost for separation and recovery of the solvent.

[0021] The mixed dope to be used can be produced by various methods, for example, a method comprising the steps of suspending a solid polyethylene in a solvent, followed by stirring at high temperature, and a method comprising the step of treating the suspension solution using a twin screw extruder equipped with mixing and conveying sections.

[0022] A dope filament is obtained by extruding the mixed dope through a spinneret equipped with arranged plural orifices. The temperature at which the mixed dope is converted into the dope filament must be selected from the temperature higher than a melting point. Of course, the melting point depends on the solvent and the concentration selected, and is at least 140° C. or higher, and more preferably at least 150° C. or higher. Of course, this temperature is selected from the temperature lower than a decomposition temperature of polyethylene.

[0023] In the method of the present invention, the dope filament is cooled with a preliminary rectified gas, or a liquid. The gas used in the present invention may be an air, or an inert gas such as nitrogen or argon. Water or the like is used as the liquid in the present invention.

[0024] In the method of the present invention, a high strength polyethylene fiber can be produced by removing the solvent from the cooled dope filament and then drawing the filament, or simultaneously performing removal of the solvent and drawing, and optionally performing multistep drawing. To obtain a fiber having the desired strength, the draw ratio is 10 times or more, preferably 12 times or more, and more preferably 15 times or more. At this time, the residual amount of the solvent in the yarn is considered as

an important parameter and is preferably 5 ppm or more. When the residual amount of the solvent in the yarn is less than 5 ppm, yarn breakage occurs very often during the process of the drawing. It is possible that the residual solvent serves like a plasticizer. When the above residual amount of the solvent is 10,000 ppm or more, it may be problematic since residual odor is left in the final product. The residual amount of the solvent is preferably within a range from 20 to 3,000 ppm.

[0025] A deformation rate of the fiber during drawing is considered as an important parameter. If the deformation rate of the fiber is too large, the breakage of the fiber occurs before arriving at a sufficient deformation rate and it is unfavorable. Also, if the deformation rate of fiber is too small, a molecular chain is relieved during drawing and the fiber having excellent physical properties can not be obtained unfavorably, although the fiber becomes thin by drawing. The deformation rate is preferably from 0.005 sec^{-1} or more and 0.5 sec^{-1} or less, and more preferably from 0.01 sec^{-1} or more and 0.1 sec^{-1} or less. The deformation rate can be calculated from the draw ratio of the fiber, the drawing rate and the length of a heating section of an oven. Namely, the deformation rate (sec^{-1}) is [1−(1/draw ratio)]× drawing rate/length of heating section.

[0026] The ultrahigh molecular weight polyethylene fiber produced by such a method shows the following characteristics. Namely, the size of a crystal derived from a monoclinic crystal is 9 nm or more, preferably 10 nm or more, and particularly preferably 12 nm or more. The strength of the fiber is preferably 30 cN/dtex.

[0027] The measuring method and the measurement conditions for characteristics of the fiber of the present invention will now be described.

(Method for Evaluation of Monoclinic Crystal Size)

[0028] The crystal size was measured using an X-ray diffraction method. RINT 2500 manufactured by Rigaku Corporation was used for the measurement. A copper anticathode was selected as an X-ray source. The operation power was 40 kV 200 mA. A collimator was set to 0.5 mm and a fiber was mounted in a fiber sample stage, and then X-ray diffraction intensity distribution was measured by scanning a counter in an equator direction. At this time, the measurement was conducted at a resolving power 2θ/θ of 0.02°. In addition, ½° was selected with regard to a light receiving slit in both cases of longitudinal and lateral limitations. The crystal size (ACS) was calculated from a half width β of a diffraction profile using the Scherrer's formula [Formula 2] shown below.

$$ACS=0.9\lambda/\beta_0 \cos\theta \qquad \text{[Formula 2]}$$

where $\beta_0=(\beta_2-\beta s)\hat{}0.5$

[0029] In the formula, λ donates a wavelength of X-ray used and 20 donates a diffraction angle. βs donates a half width of X-ray beam itself measured using a standard sample. β_2 donates a half width of a diffraction profile of a sample to be measured. A Si powder was used as the standard sample.

[0030] The crystal size of the monoclinic crystal can be determined from a line width of a diffraction spot attributed to monoclinic (010) using the Scherrer's formula. The half width was determined by fitting of the resulting diffraction curve using the Lorenz function. Grams was used as a fitting software. Since scattering attributed to amorphous was not observed in the resulting diffraction curve, the amorphous portion was not subtracted. Identification of a diffraction peak was conducted according to the method described in Seto et al. (Jap. J. Appl. Phys., 7, 31 (1968)).

(Intrinsic Viscosity)

[0031] A specific viscosity of each of various dilute solutions was measured in decalin at 135° C. by an Ubbelohde type capillary viscometer. An intrinsic viscosity was then decided from an extrapolated point into an origin of a straight line obtained by least squares approximation of points each of which reflects the value obtained by dividing the specific viscosity by the concentration of each solution to the concentration of the solution. Measurement was done with the solution prepared by adding an antioxidant (YOSHINOX™ BHT, manufactured by Yoshitomi Seiyaku K.K.) to each sample in the amount of 1% by weight based on the polymer, dissolving it while stirring at 135° C. for 24 hours.

(Viscosity Index)

[0032] Regarding a polyethylene solvent which is not described in the document such as "Polymer Handbook Fourth Edition", a viscosity index is determined by the following method.

[0033] A solution is prepared by dissolving polyethylene having a known weight average molecular weight of 50,000 or more and molecular weight distribution having a single peak of 8 or less in a solvent. At this time, an antioxidant (YOSHINOX™ BHT, manufactured by Yoshitomi Seiyaku K.K.) was added in the amount of 1% by weight based on the polymer. Then, the intrinsic viscosity is determined in the same manner as described above. The same measurement is conducted using at least three polyethylenes each having a different weight average molecular weight for determining intrinsic viscosity. Then double logarithmical plotting of the intrinsic viscosity to the weight average molecular weight is conducted. The viscosity index was determined by a gradient of a straight line obtained by least squares approximation of the logarithmical plotting.

(Strength and Elastic Modulus of Fiber)

[0034] Physical properties of the fiber of the present invention were determined by the following procedures. Using "TENSILON" manufactured by Orientec Co., Ltd., a stress-strain curve was measured in an atmosphere at a temperature of 20° C. and a relative humidity of 65%, and then the strength (cN/dtex) and elongation (%) were determined by calculating from the stress and elongation at breakage. Also, an elastic modulus (cN/dtex) was determined by calculating from a tangent line which gives the greatest gradient in the vicinity of the origin of the curve. Each value was determined by averaging ten measured values. In order to prevent sliding of the fiber during the test, a tire cord type tensile jig was used in the test.

[0035] Fineness was measured by the following procedure. Each single yarn having a length of about 2 m was prepared and the weight of the single yarn having a length of 1 m was measured and then converted in terms of 10,000 m to obtain a fineness (dtex).

(Residual Concentration of Solvent in Yarn)

[0036] The residual concentration of the solvent in the yarn in the present invention is measured using "Gas Chromatography" (GC-2014) manufactured by Shimadzu Corporation. First, 10 mg of a sample yarn was set to a glass insert of a gas chromatography injection port. Subsequently, the injection port is heated to the temperature higher than a boiling point of a solvent and then the solvent generated by heating is introduced into a column by nitrogen purging. The column temperature was set to 40° C. and the solvent is trapped for 5 minutes. Then, the column temperature was raised to 80° C. and the measurement was started. The residual concentration of the solvent was determined from the resulting peak.

[0037] The present invention will now be described by way of examples. However, it should not be construed as being limited to these examples.

EXAMPLE 1

[0038] A mixed solvent prepared by preliminary mixing decahydronaphthalene and 1-octanol in a mixing weight ratio of 50:50 was mixed with an ultrahigh molecular weight polyethylene having an intrinsic viscosity of 21.0 dL/g in a mixing weight ratio 3:97 to form a slurry-like liquid. While dispersing, the substance was dissolved in a mixer type kneader equipped with two stirring blades set at a temperature of 160° C. to form a gel-like substance. Without cooling the gel-like substance, the substance was filled into a circular cylinder set at a temperature of 185° C. and then extruded through a spinneret with one hole having a diameter of 0.8 mm set at a temperature of 170° C. at an extrusion rate of 0.8 g/min. The extruded dope filament was cooled by putting in a water bath through an air gap of 7 cm, and then taken up at a spinning rate of 20 m/min without removing the solvent. Then, the dope filament was vacuum dried under the conditions of 40° C. for 24 hours to remove the solvent. At this time, it was confirmed that the residual concentration of the solvent in the dope filament is not less than 5 ppm. The resulting fiber was brought into contact with a metal heater set to 130° C., drawn at a draw ratio of 6 times, and then a drawn yarn was taken up. Then, the drawn yarn was further drawn at 149° C. and the draw ratio was measured immediately before the breakage of the yarn, and the value thus obtained was taken as a maximum draw ratio. The maximum draw ratio was 17.5 times. Various physical properties of the resulting polyethylene fiber are shown in Table 1.

[0039] It was found that the resulting fiber shows a large maximum draw ratio and has strength and high elastic modulus.

EXAMPLE 2

[0040] In the same manner as in Example 1, except that the mixing ratio of decahydronaphthalene to 1-octanol was 96:4, a fiber was obtained. The maximum draw ratio was 15.5 times.

COMPARATIVE EXAMPLE 1

[0041] In the same manner as in Example 1, except that a dope filament was obtained using tetralin as a solvent for polyethylene, a fiber was obtained. The maximum draw ratio was 8.0 times.

COMPARATIVE EXAMPLE 2

[0042] According to the method for producing a polyethylene fiber described in the specification of WO00/24952 (PCT/NL99/00099), a dope filament was obtained using decalin and paraffin as a solvent for polyethylene. In the same manner as in Example 1, except for the above operation, a fiber was produced. When the fiber was drawn, the maximum draw ratio was 15.0 times.

TABLE 1

	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Solvent having a viscosity index of 0.6 or more	Decalin	Decalin	Tetralin	Decalin, Paraffin
Solvent having a viscosity index of 0.6 or less	1-octanol	1-octanol	None	None
Weight fraction of solvent having a viscosity index of 0.6 or more (%)	50	96	100	100
Weight fraction of solvent having a viscosity index of 0.6 or less (%)	50	4	0	0
Maximum draw ratio (—)	18.0	15.5	8.0	15.0
Fineness (dtex)	0.6	0.9	1.5	0.9
Strength (cN/dtex)	44	33	27	27
Elastic modulus (cN/dtex)	1221	1090	604	720
Residual amount of solvent having a viscosity index of 0.6 or more in yarn (ppm)	180	84	70	4340
Residual amount of solvent having a viscosity index of 0.6 or less in yarn (ppm)	188	11	0	0
Crystal size of monoclinic crystal (nm)	13.4	9.2	7.2	8.1

[0043] The fiber obtained by a method for producing a high strength polyethylene fiber of the present invention can be widely used for industrial applications, for example, high performance textiles such as various sport wears, bullet-proof/protective wears and protective gloves, and various safety goods; various rope products such as tag ropes, mooring ropes, yacht ropes, and building ropes; various braid products such as fishing lines and blind cables; net products such as fishing nets and ball-protecting nets; reinforcing materials for chemical filters and battery separators; various nonwoven fabrics; curtain materials such as tents; reinforcing fibers for sport goods such as helmets and ski boards; and reinforcing fibers for composite products such as speaker cones, concrete reinforcing, and prepregs.

1. A high strength polyethylene fiber, comprising a crystal derived from a monoclinic crystal having a size of 9 nm or more.

2. The high strength polyethylene fiber of claim **1**, wherein the fiber has a tensile strength of 30 cN/dtex or more.

3. The high strength polyethylene fiber of claim **1**, which is produced by mixing an ultrahigh molecular weight polyethylene having an intrinsic viscosity of 8 dL/g or more with a mixed solvent comprising solvent (A) as a good solvent for

polyethylene and solvent (B) as a poor solvent for polyethylene in a mixing ratio of solvent (A) to solvent (B) within a range from 20:80 to 99:1 by weight to form a mixed dope having a polyethylene concentration of 0.5% by weight or more and less than 50% by weight, extruding the dope through an orifice, cooling the extruded dope, and drawing it into a filament yarn.

4. The high strength polyethylene fiber of claim **3**, wherein solvent (A) has a viscosity index for polyethylene of 0.6 or more, and solvent (B) has a viscosity index for polyethylene of 0.6 or less.

5. The high strength polyethylene fiber of claim **1**, which contains 5 ppm or more of a solvent having a viscosity index for polyethylene of 0.6 or less.

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