(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 818 380 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
07.10.2026 Bulletin 2026/41

(21) Application number: **24896503.0**

(22) Date of filing: **26.11.2024**

(51) International Patent Classification (IPC):
D01D 5/04 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
D01D 5/04; D01D 5/14; D01F 6/04

(86) International application number:
PCT/CN2024/134396

(87) International publication number:
WO 2025/113414 (05.06.2025 Gazette 2025/23)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **30.11.2023 CN 202311634293**

(71) Applicants:
- **China Petroleum & Chemical Corporation**
  Beijing 100728 (CN)
- **Sinopec Yizheng Chemical Fibre Co., Ltd.**
  Yangzhou, Jiangsu 211900 (CN)

(72) Inventors:
- **HU, Ting**
  Yangzhou, Jiangsu 211900 (CN)
- **SHI, Yunhu**
  Yangzhou, Jiangsu 211900 (CN)
- **YANG, Yong**
  Yangzhou, Jiangsu 211900 (CN)
- **CHEN, Zhiming**
  Yangzhou, Jiangsu 211900 (CN)
- **LI, Jinping**
  Yangzhou, Jiangsu 211900 (CN)
- **QIAO, Xiujing**
  Yangzhou, Jiangsu 211900 (CN)

(74) Representative: **karo IP**
Patentanwälte PartG mbB
Steinstraße 16-18
40212 Düsseldorf (DE)

(54) HIGH-MOLECULAR-WEIGHT POLYMER MONOFILAMENT WITH ULTRA-LOW RESIDUAL SOLVENT CONTENT, AND MANUFACTURING METHOD THEREFOR AND USE THEREOF

(57) The present invention relates to a high molecular weight polymer monofilament with ultra-low solvent residue, a process for producing the same, and use thereof. The process for producing the high molecular weight polymer monofilament according to the present invention comprises subjecting a filament precursor comprising a high molecular weight polymer and a solvent to an ambient atmosphere as follows: the ambient atmosphere has an elevated temperature, and the concentration of the solvent in the ambient atmosphere is 50 vol% or more, based on the total volume of the ambient atmosphere as 100 vol%. The high molecular weight polymer monofilament according to the present invention has the feature of an ultra-low solvent residue, and is particularly suitable for use in manufacturing medical products.

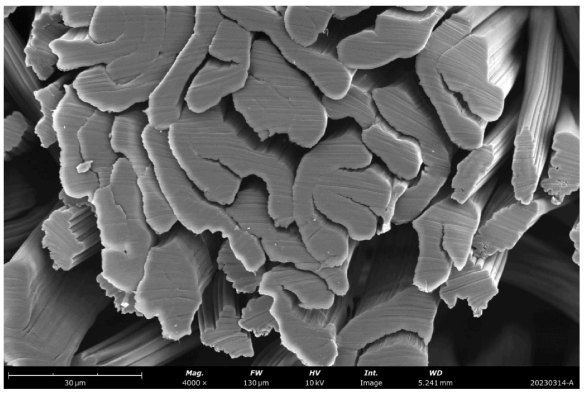


Fig. 1

EP 4 818 380 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to the field of high-performance fibers, and specifically, to a high molecular weight polymer monofilament with ultra-low solvent residue, a process for producing the same, and use thereof.

BACKGROUND ART

[0002] Existing production technologies for ultra-high molecular weight polyethylene fiber are divided into two major categories: a wet spinning process using white oil as a solvent and a dry spinning process using decahydronaphthalene as a solvent. The former process requires solvent extraction followed by evaporation, such that the process is complicated, and the product has high solvent residue, resulting in insufficient purity of the product so that it cannot be applied in the medical field. With the latter process, it is difficult for the existing technology to achieve an extremely low residual level of the solvent inside the fiber through evaporation, and hardly satisfy the application requirements in the medical field. Meanwhile, for medical applications, to ensure the fiber being sufficiently pure and does not cause other adverse reactions, the fiber surface cannot be treated in any way; therefore, the monofilaments tend to disperse, have poor cohesion, and are difficult to process in medical applications.

SUMMARY OF THE INVENTION

[0003] Ultra-high molecular weight polyethylene fibers are prone to static electricity due to friction during processing and production. Therefore, in the process of producing fiber, the cohesion problem is usually solved by adding antistatic agents, surface coating with oil agents, etc., to achieve the ideal processing and use effect of the fiber. However, such methods lead to complex fiber composition and insufficient purity, and for medical applications, especially under conditions such as permanent implantation into the human body, it is likely to cause adverse reactions. The fiber of the present invention can achieve an ideal cohesion state without surface treatments such as oiling, ensuring the cleanliness of implantable medical-grade ultra-high molecular weight polyethylene fibers.

[0004] The spinning process differs from the conventional gel spinning method for ultra-high molecular weight polyethylene fibers, and instead adopts a dry-state coagulation method. The spinning shaping does not involve a process of cooling gel, does not form a gel-state as-spun filament, and directly enters a flash solidification stage to form a dry-state as-spun filament precursor, whereby the solvent residue reaches an extremely low level, ensuring the cleanliness of the product.

[0005] According to a first aspect of the present invention, it relates to a process for producing a high molecular weight polymer monofilament (particularly an ultra-high molecular weight polyethylene monofilament), comprising subjecting a filament precursor (particularly a spinning dope stream) comprising a high molecular weight polymer (such as ultra-high molecular weight polyethylene) and a solvent (such as decahydronaphthalene) to an ambient atmosphere as follows: the ambient atmosphere having an elevated temperature (called as ambient temperature), and the concentration of the solvent in the ambient atmosphere being 50 vol% or more (preferably 80 vol% or more, 85 vol% or more, 90 vol% or more, or 95 vol% or more), based on the total volume of the ambient atmosphere as 100 vol%.

[0006] According to a second aspect of the present invention, it relates to an ultra-high molecular weight polyethylene monofilament, which has a polyethylene molecular chain entanglement degree of 0%-50% (preferably 1%-20%), and a spinning solvent content of 500 ppm or less (preferably 100 ppm or less, 50 ppm or less, 10 ppm or less, or 1 ppm or less), relative to the total weight of the ultra-high molecular weight polyethylene monofilament as 100 wt%.

[0007] According to a third aspect of the present invention, it relates to an ultra-high molecular weight polyethylene multifilament, which is formed by bundling a plurality of (e.g., 2-10000, preferably 5-400) ultra-high molecular weight polyethylene monofilaments according to the present invention or ultra-high molecular weight polyethylene monofilaments produced by the process according to the present invention, wherein in the ultra-high molecular weight polyethylene multifilament, 50% or more (preferably 60% or more, 70% or more, 80% or more, or 90% or more) of the total number of the ultra-high molecular weight polyethylene monofilaments are in an embedded-interlocked state.

[0008] According to a fourth aspect of the present invention, it relates to a medical product comprising the ultra-high molecular weight polyethylene monofilament according to the present invention, the ultra-high molecular weight polyethylene multifilament according to the present invention or an ultra-high molecular weight polyethylene monofilament produced by the process according to the present invention.

TECHNICAL EFFECT

[0009] The present invention provides a fiber having an irregularly flat and elongated monofilament cross-section, being in a flattened or bent and folded state, with the monofilaments being in an embedded-interlocked state. This interlocking fiber has high strength, extremely low solvent residue, and a single and pure component, and is particularly suitable for medical use.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

Fig.1 is a microscopic topography diagram of the fiber.

Fig.2 is a structural schematic diagram of the spinning forming zone.

Fig.3 is a schematic diagram showing the principle of the formation of the fiber cross-sectional morphology.

EMBODIMENTS

[0011] The embodiments of the present invention will be illustrated in more detail below, but it should be understood that the scope of the invention is not limited by the embodiments, but is defined by the claims appended.

[0012] All publications, patent applications, patents, and other references mentioned in this specification are herein incorporated by reference in their entirety. Unless defined otherwise, all technical and scientific terms used herein are understood same as the meanings commonly known to those skilled in the art. In case of conflict, definitions according to the present specification will control.

[0013] When the specification introduces materials, substances, processes, steps, devices, components, or the like initiated with "known to those ordinary skill in the art", "prior art", or the like, it is intended that the subject matter so initiated encompass not only those conventionally used in the art at the time of filing this application, but also those may not be so commonly used at the present time, but will become known in the art as being suitable for a similar purpose.

[0014] In the context of the present invention, all numerical values of a parameter (e.g., quantity or condition) are to be understood as being modified in all instances by the term "about", whether or not "about" actually appears before the numerical value.

[0015] In the context of the present invention, each device used in the present invention may adopt a structure conventionally selected in the art without being particularly limited thereto.

[0016] In the context of present invention, the term "substantially" means a deviation acceptable or considered as reasonable by a person skilled in the art, such as within $\pm$ 2%, within $\pm$ 1%, within $\pm$ 0.5% or within $\pm$ 0.1%. Furthermore, "substantially free of", "substantially no", or similar expressions mean "completely free of" or "none at all" under ideal circumstances, but do not exclude minimal installation or presence for production safety or personal protection.

[0017] In the context of the present invention, the method for measuring the solvent concentration in the ambient atmosphere is gas chromatography, with a vaporization temperature of 250°C, a column box and column temperature of a constant temperature at 130°C; carrier gas: nitrogen; pre-column pressure: about 73.5 kPa (0.75 kgf/cm^2); and flow rate: 35 ml/min (post-column pressure).

[0018] In the context of the present invention, the method for measuring the polyethylene molecular chain entanglement degree is the DSC method comprising: first heating to 154°C, holding isothermally for 15 min, then cooling to room temperature at 10°C/min, and then heating to 180°C at 10°C/min; wherein the area ratio of the high-temperature peak is calculated as the entanglement degree.

[0019] In the context of the present invention, the method for measuring the fiber modulus is GB/T19975.

[0020] In the context of the present invention, the method for measuring the linear density deviation is GB/T14343.

[0021] In the context of the present invention, the method for measuring the inter-monofilament adhesion density comprises: using electron microscopy to measure 10 fibers, respectively measure the proportion of bond length within a 160 μm range, and calculate the average value.

[0022] In the context of the present invention, the method for measuring the surface atomic concentration is performed using a Phi Quantum 2000 device. The sample is prepared by winding the filaments around a metal sample holder. In each analysis, a plurality of filaments (defined by the analysis area) is measured. Each sample is measured at two positions. During the measurement, the angle between the axis of the analyzer and the sample surface is 45°; and the information depth is then about 5 nm. Monochromatic AlKα radiation is used, the measurement spot is 100 μm; and the measurement area is 800 $\times$ 400 μm. Elements present on the surface have been identified by wide-scan measurement. The chemical state and concentration of the elements are determined by narrow-scan measurement. The peak areas are converted into atomic concentrations using standard sensitivity factors.

[0023] In the context of the present invention, the method for measuring the spinning solvent content is GB/T41671-2022.

[0024] In the context of the present invention, the method for measuring the monofilament fineness comprises GB/T3916-2013.

[0025] In the context of the present invention, the method for measuring the fiber strength is GB/T19975-2005.

[0026] In the context of the present invention, the method for measuring the polyethylene crystallinity comprises: using a Diamond DSC differential scanning calorimeter from PerkinElmer company, USA, to convert crystallinity through thermal analysis. 8-9 mg of sample is weighed, and the experiment is conduct under nitrogen protection. Heat from 40°C to 170°C at a rate of 10°C/min, hold at a constant temperature for 5 min to eliminate thermal history; then cool to 40°C at rates of 2.5, 5, 10, 20, 40°C/min respectively to obtain cooling curves; and then heat to 160°C at 10°C/min to obtain a second heating curve. The crystallinity is calculated with a formula of $Xc = \Delta H/\Delta H0$, where ΔH is the melting enthalpy from the second heating curve, J/g; and $\Delta H0$ is the melting en-

thalpy for 100% crystallinity, $\Delta H0 = 293$ J/g.

[0027] In the context of the present invention, free state refers to an observation state of the fiber under completely undisturbed conditions.

[0028] In the context of the present invention, an average unfolded width refers to straightening the cross-section of the fiber monofilament to reach a maximum width; measure the maximum width of ten monofilaments and take the average value as the average width.

[0029] In the context of the present invention, a central average thickness refers to drawing the cross-section of the fiber monofilament straight to reach a maximum width, drawing two parallel tangent lines at the maximum point in the thickness direction along the outer contour of the monofilament cross-section, and measuring the distance between the parallel lines as the thickness of this monofilament. Measure the thickness of ten monofilaments and take the average value as the average thickness.

[0030] In the context of the present invention, an end average thickness refers to the average value of the thicknesses at both ends in the width direction of the fiber monofilament.

[0031] In the context of the present invention, embedded-interlocked means that the fiber monofilaments are not laid flat together, but are nested and crossed with each other, as shown in Fig.1.

[0032] In the context of the present invention, not detected means that the detected amount is below the detection limit, typically less than 1 ppm.

[0033] In the context of the present invention, the fiber color hue is tested using a spectrophotometer (test instrument Data Color 850).

[0034] In the context of the present invention, the creep elongation rate is tested by weaving the fiber into a suture of uniform diameter (No. 2 thread is recommended) and testing at 40°C, 40% load condition for 672 h (28 days).

[0035] In the context of the present invention, the short-chain branch content of the ultra-high molecular weight polyethylene is tested using high-temperature GPC-IR (test instrument being Polymer Char). The chromatograph is equipped with a high-sensitivity IR5-MCT detector, wherein the chromatographic column is a GPC rapid column (250 mm × 10 mm), and the column temperature is 160°C, with 1,2,4-trichlorobenzene containing 0.3 g/L of 2,6-di-tert-butyl-p-cresol as the mobile phase, a flow rate of 1 ml/min, a column temperature of 160°C, a sample injection volume of 200 μL, and a time of 15 min; where each sample is analyzed twice.

[0036] All percentages, parts, ratios, and the like referred to in the specification are based on weight, and pressures denote gauge pressures unless explicitly indicated.

[0037] In the context of the present invention, any two or more embodiments or aspects of the present invention may be arbitrarily combined, and the technical solutions resulted are part of the original disclosure of the present specification, and also fall within the scope of the present invention.

[0038] An embodiment according to the present invention relates to a high molecular weight polymer monofilament, particularly an ultra-high molecular weight polyethylene monofilament. The monofilament according to the present invention can be used in the medical field, and can also be used in fishing lines, gloves, ballistic protection, ropes and cables, net structures, knitted fabrics, etc.

[0039] According to an embodiment of the present invention, the high molecular weight polymer monofilament has a surface carbon atom concentration of 98% or more (preferably 99% or more, 99.5% or more, or substantially 100%), and a surface oxygen atom concentration of 2% or less (preferably 1% or less, 0.5% or less, or not detected). The inventors of the present invention have found that the lower the concentration of oxygen atoms, the cleaner the fiber surface, and the more suitable it is for medical applications. More preferably, the high molecular weight polymer monofilament does not comprise a spinning finishing agent or residue thereof on its surface or inside.

[0040] According to an embodiment of the present invention, the high molecular weight polymer monofilament has a spinning solvent content of 500 ppm or less (preferably 100 ppm or less, 50 ppm or less, 10 ppm or less, or 1 ppm or less), relative to 100 wt% of the total weight of the high molecular weight polymer monofilament. The inventors of the present invention have found that solvent residue easily causes cell wall rupture and damage, resulting in the cytotoxicity test fail, and the fiber cannot meet medical requirements. Therefore, the lower the solvent residue, the purer the fiber, and the more suitable it is for medical applications.

[0041] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a polyethylene molecular chain entanglement degree of 0%-50% (preferably 1%-20%). The inventors of the present invention have found that a too low entanglement degree will cause the molecular chains to slip easily when the fiber is under stress, resulting in large creep or strength failure; while a too high entanglement degree will cause difficulties in spinning, a large number of broken filaments or defects during the drawing process, and uneven fiber strength.

[0042] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a monofilament fineness of 0.5-10 dtex (preferably 0.55-3.0 dtex), and a fiber strength of 5-45 cN/dtex (preferably 20-40 cN/dtex). The inventors of the present invention have found that without surface treatment of the fiber, it is difficult to carry out high-ratio stretching; the fiber will break during stretching due to problems such as static electricity and fluffing, so as to be difficult to form filaments. The technology of the present invention solves this problem well, by which not only filaments can be formed, but also the monofilaments are self-locking and interlocking through nesting, forming

high-strength monofilaments during the stretching process, meeting medical applications, especially for use in braided sutures, and can withstand large tensile forces during use.

[0043] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a fiber modulus of ≥750 cN/dtex (preferably 800-1800 cN/dtex). The inventors of the present invention have found that the fiber modulus needs to be within a reasonable range. If the modulus is too low, the orientation is insufficient, and the strength also decreases; while if the modulus is too high, the fiber is stiff, and the woven thread or cloth is hard and not soft, which is difficult to bend or knot.

[0044] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a linear density deviation of ≤20% (preferably ≤10%), and an inter-monofilament adhesion density of ≤100% (preferably ≤50%, preferably ≤10%, preferably ≤1%). The inventors of the present invention have found that adhesion of monofilaments easily causes a large linear density deviation of the monofilaments, poor fiber consistency, and affects the uniformity of subsequent processing; such that adhesion should be avoided as much as possible.

[0045] According to an embodiment of the present invention, the high molecular weight polymer monofilament has a crystallinity of ≥50% (preferably ≥70%). The inventors of the present invention have found that the higher the crystallinity of the monofilament, the higher the fiber strength. According to the present invention, without surface treatment of the fiber, through nested self-locking interlocking between monofilaments, high-ratio stretching can be tolerated, and high crystallinity can be achieved.

[0046] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a cross-section (a cross-section as grown) in a free state that is a flat and elongated arc shape. This flat and elongated arc shape is naturally formed during the manufacturing process of the monofilament, rather than being caused by post-processing or treatment. The monofilament cross-section is arc-shaped, making it easy to nest and cross with each other, and through high-ratio stretching, a tight interlocking effect is achieved.

[0047] According to an embodiment of the present invention, the cross-section has an average unfolded width of 10 μm or more (preferably 15-100 μm or 20-60 μm), and the cross-section has an average thickness of 2 μm or more (preferably 3-20 μm or 5-10 μm). The ultra-high molecular weight polyethylene fibers produced by prior art generally have a circular or nearly circular cross-section, with a fiber diameter of 16 μm or more, such that the monofilaments cannot nest with each other. The monofilament according to the present invention has a thickness less than the width, which thus can be easily concaved and bent, forming mutual nesting and self-locking, and also increases the surface area of the monofilament, such that the volatilization surface for removing the solvent is large, and the solvent residue is extremely low.

[0048] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a ratio of the average unfolded width of the cross-section to the average thickness of the cross-section of 2 or more (preferably 3-100 or 4-20).

[0049] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene monofilament has a ratio of the central average thickness of the cross-section to the end average thickness of the cross-section of less than 1 (preferably ≤0.5). The fiber cross-section exhibits a shape with thick ends and a thin middle, making it easier to achieve concavity and mutual nesting.

[0050] According to an embodiment, the invention further relates to an ultra-high molecular weight polyethylene multifilament, which is formed by bundling a plurality of (e.g., 2-10000, preferably 5-400) ultra-high molecular weight polyethylene monofilaments according to any aspect of the present invention described above or below. According to the present invention, in the ultra-high molecular weight polyethylene multifilament, 50% or more (preferably 60%, 70% or more, 80% or more, or 90% or more) of the total number of the ultra-high molecular weight polyethylene monofilaments are in an embedded-interlocked state. Through side blowing, the monofilament cross-section becomes arc-shaped, easily nesting and crossing with each other, and then through the high-ratio stretching, a tight interlocking effect is achieved. The embedded-interlocked between monofilaments solves the problem of the fiber being easily dispersed and fluffed without surface treatment, giving the fiber excellent processability.

[0051] Fig.1 schematically shows a microscopic topography diagram of the fiber of the present invention, clearly showing the tight embedded-interlocked state between the fiber monofilaments.

[0052] According to an embodiment of the present invention, after the bundling, the obtained ultra-high molecular weight polyethylene multifilament is stretched (multifilament stretching) in one or more stages (e.g., 1-8 or 2-5 stages). Multifilament stretching can stretch the monofilaments in a mutually embedded-interlocked state, improving the stretching tolerance of the monofilaments under high-ratio stretching conditions. At the same time, due to high-ratio stretching, the cross-sections of the monofilaments become narrower, tightly squeezed, achieving a better interlocking effect.

[0053] According to an embodiment of the present invention, the operating conditions of the multifilament stretching comprise: a stretching temperature of 90-160°C (preferably 120-140°C), and a (total) stretching ratio of 2-200 (preferably 10-30).

[0054] According to an embodiment of the present invention, the invention further relates to a process for

producing a high molecular weight polymer monofilament, particularly a process for producing an ultra-high molecular weight polyethylene monofilament. According to the present invention, the process can be used to produce the ultra-high molecular weight polyethylene monofilament according to the present invention, but the process for producing the high molecular weight polymer monofilament according to the present invention is not limited thereto.

[0055] According to an embodiment of the present invention, the process for producing the high molecular weight polymer monofilament comprises subjecting a filament precursor comprising a high molecular weight polymer and a solvent to a specific ambient atmosphere. Here, the filament precursor, as it contains a relatively large amount of solvent, is also often called as a wet-state filament precursor. The inventors of the present invention have found that by subjecting the filament precursor to the specific ambient atmosphere, the molecular chains inside the fiber are entangled to a certain extent, forming a certain degree of entanglement, which can effectively reduce the slip between molecular chains.

[0056] According to an embodiment of the present invention, the ambient atmosphere has an elevated temperature (called as ambient temperature). In other words, the ambient atmosphere, due to energy input, causes the bulk temperature of the filament precursor to be elevated compared to its initial state. The inventors of the present invention have found that an elevated temperature facilitates accelerated entanglement, allowing the molecular chain structure inside the fiber to achieve ideal entanglement within the short spinning formation time.

[0057] According to the present invention, the concentration of the solvent (which is actually present as vapor) in the ambient atmosphere is desired to be as high as possible; however, as the ambient atmosphere is not completely closed to other atmospheres, for example, step 4) described later in the specification introduces in a large amount of blowing gas (e.g., nitrogen or carbon dioxide), which will inevitably enter the ambient atmosphere in small amounts due to back-mixing or diffusion of the gas, thereby diluting the solvent vapor in the ambient atmosphere to some extent, resulting in a decrease in the concentration of the solvent vapor; thus, it is generally impossible to achieve completely 100 vol%. Considering this practical situation, according to the present invention, preferably, the concentration of the solvent in the ambient atmosphere is 50 vol% or more (preferably 80 vol% or more, 85 vol% or more, 90 vol% or more, or 95 vol% or more), based on the total volume of the ambient atmosphere as 100 vol%. Such a high concentration of solvent vapor is strongly avoided in the spinning processes of the prior art, but the present invention breaks through this inherent thinking. The inventors of the present invention have found that in an ambient atmosphere containing a high concentration of solvent vapor, a relatively dense skin layer will not be formed on the monofilament surface due to more rapid volatilization of the solvent on the monofilament surface than the solvent inside the monofilament, which would otherwise hinder the migration and evaporation of the solvent inside the monofilament to the monofilament surface. Moreover, as the monofilament surface is always immersed in the high-concentration solvent vapor, the monofilament surface is substantially always in a dissolved state in the ambient atmosphere, and the volatilization path of the solvent contained in the monofilament from the interior to the surface is unobstructed, thereby helping the monofilament to "dry through" from the inside to outside, thus significantly reducing the solvent residue inside the monofilament (especially in the core) compared with the prior art. In addition, as the monofilament surface is substantially always in a dissolved state in the ambient atmosphere, when the initial stretching described later in this specification is performed, the polymer molecular chains on the monofilament surface are in a moving-free state, and will slide and entangle freely as the initial stretching proceeds. If a solidified (or at least semi-solidified) skin layer forms on the monofilament surface, as the polymer molecular chains in the skin layer are substantially consolidated with each other, this consolidated state will be forcibly broken during the initial stretching, resulting in macroscopic damage to the fiber's surface skin layer, forming fuzz defects; then after high-ratio stretching, broken filaments will occur on the fiber surface, affecting the smoothness of the subsequent braided thread, and also reducing the fiber strength.

[0058] According to an embodiment of the present invention, to ensure the relatively high solvent vapor concentration in the ambient atmosphere as described above in this specification to achieve the intended purpose of the present invention, as one of the most convenient implementation means, for example, substantially no diluent gas or completely no diluent gas at all is proactively or intentionally introduced into the ambient atmosphere or the region corresponding to the ambient atmosphere (e.g., the hollow cylinder or flash-solidification zone described below in this specification). The so-called diluent gas refers to any gas other than the solvent vapor, such as nitrogen or carbon dioxide. As mentioned above, the introduction of these diluent gases will reduce (dilute) the concentration of solvent vapor in the ambient atmosphere. Furthermore, the inventors of the present invention have found that the introduction (proactive introduction) of these diluent gases may also cause wind disturbance problems. Specifically, the inventors of the present invention have found that under no-wind-disturbance conditions, the monofilament cross-section is isotropic, nearly circular; such that in the next step of wind-shaping, monofilaments have small differences between each other, and eare more consistent with reduced unevenness. If there are wind disturbance conditions, the monofilament is weaker here and easily deformed; then during further wind-shaping, the unevenness of the monofilament cross-section worsens, ultimately producing the fiber consistency worse. In addition, according to

the present invention, the solvent vapor leaves step 3) together with the dry-state filament precursor in a direction substantially parallel to the direction of the initial stretching. According to the present invention, the so-called proactive or intentional introduction means a dedicated gas inlet being set in the ambient atmosphere or being set for the ambient atmosphere to use the flowing gas input to quickly blow away the solvent vapor in the ambient atmosphere, thereby accelerating solvent evaporation; which is a conventional arrangement in the prior art.

[0059] According to an embodiment of the present invention, depending on practical needs, a certain amount of solvent vapor may also be intermittently or continuously input into the ambient atmosphere to ensure that the concentration of the solvent in the ambient atmosphere reaches the numerical range specified in the present invention. According to this embodiment, the process according to the present invention can treat ultra-high molecular weight polyethylene gel filaments obtained by conventional gel spinning processes, and then use such gel filaments to produce the high molecular weight polymer monofilament with ultra-low solvent residue of the present invention.

[0060] According to an embodiment of the present invention, the step 3) is carried out in a hollow cylinder. Here, the hollow cylinder comprises a top opening, a bottom opening, and a side wall (i.e., shell) connecting the top opening with the bottom opening and formed around the central axis of the hollow cylinder. According to an embodiment of the present invention, the top opening may be sealingly connected to the spinneret, whereby the filament precursor leaves the hollow cylinder through the bottom opening. Additionally, a heating member may be provided on at least a part of the side wall to allow the temperature of the inner cavity of the hollow cylinder to reach the ambient temperature. Preferably, as mentioned above, substantially no diluent gas or completely no diluent gas at all is proactively or intentionally introduced into the hollow cylinder, for example, no purge air inlet conventionally provided in the prior art is provided on the side wall.

[0061] According to an embodiment of the present invention, the ambient temperature is higher than the boiling point of the solvent (preferably 0.1-150°C, 0.2-100°C, 0.4-50°C, 0.5-20°C, 0.5-10°C, or 0.5-5°C higher than the boiling point of the solvent). The inventors of the present invention have found that a higher ambient temperature is favorable for solvent evaporation. However, if the temperature is too high, the molecular structure of the fiber will be damaged, reducing the fiber strength; while if the temperature is too low, the solvent concentration in the ambient atmosphere will decrease, forming a skin layer.

[0062] According to an embodiment of the present invention, the high molecular weight polymer can be any polymer with a relatively high molecular weight (e.g., a viscosity-average molecular weight of generally 500,000 or 1,000,000 or more) that can be spun by a solvent spinning method, such as ultra-high molecular weight polypropylene or ultra-high molecular weight acrylic polymers, and particularly ultra-high molecular weight polyethylene can be exemplified.

[0063] According to an embodiment of the present invention, the process for producing the high molecular weight polymer monofilament comprises step 1): mixing the high molecular weight polymer with a solvent to prepare a spinning dope.

[0064] According to an embodiment of the present invention, relative to 100 parts by weight of the ultra-high molecular weight polyethylene, the amount of the solvent used is at most 2000 parts by weight (preferably 1000-1500 parts by weight).

[0065] According to an embodiment of the present invention, there is no particular limitation on the solvent, and any type conventionally known in the art may be used, but generally at least one selected from the group consisting of white oil, mineral oil, naphthalene, decahydronaphthalene, tetrahydronaphthalene, kerosene, xylene, toluene, petroleum fractions, halogenated hydrocarbons, cycloalkanes, and cycloolefins, preferably decahydronaphthalene.

[0066] According to an embodiment of the present invention, there is no particular limitation on the ultra-high molecular weight polyethylene, and any type conventionally known in the art may be selected, but its viscosity-average molecular weight is generally 1,000,000 to 9,000,000, preferably 3,000,000 to 7,000,000.

[0067] According to an embodiment of the present invention, the ultra-high molecular weight polyethylene (raw material) has a crystallinity of ≥30% (preferably ≥40%).

[0068] According to an embodiment of the present invention, there is no particular limitation on the short-chain branch content of the ultra-high molecular weight polyethylene. For example, the number of short-chain branches per 1000 skeletal carbon atoms can be any value between 0 and 100. However, from the perspective of improving the creep resistance of the final monofilament or fiber, it is preferable to comprise 3-100 (preferably 3-30) short-chain branches per 1000 skeletal carbon atoms. Here, the so-called short-chain branches refer to alkyl branches having 1-4 carbon atoms. In addition, by using ultra-high molecular weight polyethylene with a short-chain branch content meeting the requirements of the present invention for spinning, the monofilament or fiber of the present invention can have a creep elongation rate of ≤10% (preferably ≤5%).

[0069] According to an embodiment of the present invention, provided that the intended use of the present invention (particularly medical use) is met, the spinning dope may also include additives such as pigments, thereby producing colored filaments. Here, as the pigment, from the viewpoints of compatibility and coloring effect, inorganic pigments such as cobalt chrome blue, chro-

mium oxide, carbon black, titanium dioxide, etc., are preferred due to their good coloring effect and biological safety. In addition, the amount of the pigment added is not more than 10 wt%, preferably not more than 2 wt%, based on the weight of the ultra-high molecular weight polyethylene.

[0070] According to an embodiment of the present invention, the process for producing the high molecular weight polymer monofilament comprises step 2): extruding the spinning dope through a spinneret to form a spinning dope stream or the filament precursor.

[0071] According to an embodiment of the present invention, the solvent content in the filament precursor, e.g., the spinning dope stream, is 80-97 wt% (preferably 90-95 wt%), based on the total weight of the filament precursor as 100 wt%.

[0072] According to an embodiment of the present invention, in step 2), the extrusion temperature is 150-220°C (preferably 170-180°C), and the extrusion speed is 2-20 m/min (3-5 m/min).

[0073] According to an embodiment of the present invention, in step 2), the spinneret is provided with at least one spinning orifice. Here, the number of the spinning orifices may be, for example, 10-10000, such as 50-500. In addition, the cross-sectional shape of the spinning orifice may be circular or substantially circular. With such a spinning orifice, the fiber is isotropic after exiting the spinneret, and the cross-section is nearly circular; such that under the action of side wind, the morphology of the monofilaments can be more uniform and consistent. Preferably, the circular equivalent diameter of the cross-section of the spinning orifice is 0.1-3 mm (preferably 0.5-1.5 mm).

[0074] According to an embodiment of the present invention, when subjecting the filament precursor to the ambient atmosphere, the filament precursor is stretched (called as initial stretching). More specifically, the producing process comprises step 3): stretching the filament precursor or the spinning dope stream under the ambient atmosphere (called as initial stretching) to obtain a dry-state filament precursor. According to the present invention, this step is completely different from that of the general gel spinning method; wherein through rapid and large amount of evaporation of the solvent, the macromolecular chains lose the plasticizing effect of the solvent small molecules in a short time and lose their mobility, achieving the purpose of solidifying and disentangling the state, while other components is not introduced in. Without this step, the macromolecular chains will still maintain high mobility and will quickly re-entangle, resulting in further high-ratio stretching impossible. Here, as an example, depending on the type of solvent used, taking decahydronaphthalene as an example, the ambient temperature is generally 189-320°C (preferably 191-210°C). The inventors of the present invention have found that if the ambient temperature is too low, the solvent cannot be rapidly removed, failing to achieve the purpose of rapid solidification of the molecular chains; whilst if the ambient temperature is too high, the fiber solvent is prone to fusing, leading to spinning failure.

[0075] According to a preferred embodiment of the present invention, the solvent is removed from the filament precursor in the ambient atmosphere, more specifically, step 3) is carried out until the solvent content in the filament precursor reaches 1000 ppm or less (preferably 500 ppm or less, 100 ppm or less, 50 ppm or less, or 10 ppm or less). The inventors of the present invention have found that the lower the residual solvent in the filament precursor, the lower the solvent residue in the final finished fiber, and the purer the product. Above 1000 ppm, it is difficult to completely remove the residual solvent in the filament precursor during further stretching.

[0076] According to an embodiment of the present invention, in step 3), the initial stretching causes the cross-sectional shrinkage ratio of the filament precursor or the spinning dope stream to reach 10-10^6 (preferably 100-1000). A high cross-sectional shrinkage ratio will cause the solvent to rapidly migrate to the surface. If the shrinkage ratio is too low, the solvent migration is insufficient, and the residue amount is high; while if the shrinkage ratio is too high, the monofilament cannot withstand the high-ratio stretching and thus breaks. As an example, the stretch ratio of the initial stretching is generally 1-10 (preferably 3-5). The inventors of the present invention have found that if the stretch ratio is too low, the desired cross-sectional shrinkage ratio cannot be achieved; while if the stretch ratio is too high, the fiber is easy to be broken, leading to spinning failure.

[0077] According to an embodiment of the present invention, the duration that the filament precursor spends in the ambient atmosphere or the duration of the initial stretching is generally 0.5-180 s, preferably 5-60 s. The inventors of the present invention have found that if the residence time of the fiber molecular structure in the high-temperature environment is too long, entanglement is severe, producing stretching impossible; while if the residence time is too short, the solvent removal rate is too low, resulting in an impure product.

[0078] Fig.2 schematically shows a diagram of the spinning forming process, wherein three zones divided are used: the spinning dope being extruded from the spinneret and fed into an evaporation zone to remove the solvent, then fed into a wind-shaping zone for cross-section shaping, and finally fed into a stretching and seting zone to form a high molecular weight polymer monofilament (called as as-spun monofilament).

[0079] According to an embodiment of the present invention, the process for producing the high molecular weight polymer monofilament further comprises step 4): providing a blowing gas to the dry-state filament precursor, with or without stretching, to obtain an as-spun monofilament. According to the present invention, for convenience of implementation, the blowing gas may be provided to the dry-state filament precursor in a direction at a certain angle (e.g., 30-150°, preferably 60-120°, particularly preferably substantially 90°) to the traveling

direction of the dry-state filament precursor, but there is no particular limitation.

[0080] According to an embodiment of the present invention, in step 4), to obtain the specific cross-sectional shape of the monofilament according to the present invention (particularly a flat and elongated arc shape) and to substantially completely remove the residual solvent, it is preferred to provide the blowing gas to the dry-state filament precursor only from one side of the dry-state filament precursor (also called as side wind). The inventors of the present invention have found that the dry-state as-spun filament precursor has a certain plasticity under high temperature conditions, and the initial state is nearly circular. The side blowing wind leads to form a pressure difference in the vertical radial direction of the fiber, with high pressure in the middle and low pressures on both sides; while forming a flat shape, the fiber also bends inward, forming an arc. Fig.3 schematically shows a diagram of the formation principle of the monofilament cross-section. In addition, the inventors of the present invention have also found that through the blowing, the solvent content in the filament precursor can be further reduced to 100 ppm or less (preferably 50 ppm or less, 10 ppm or less, 5 ppm or less, 2 ppm or less, or 1 ppm or less).

[0081] According to an embodiment of the present invention, in step 4), the temperature of the blowing gas is 0-50°C higher (preferably 1-10°C higher) than the melting point of the dry-state filament precursor or the temperature of the blowing gas is ≥138°C (preferably 140-150°C). The inventors of the present invention have found that the temperature of the blowing gas should be greater than the melting point of the dry-state filament precursor; where if it is too high, the dry-state filament precursor will fuse and break; while if it is too low, the dry-state filament precursor has no plasticity.

[0082] According to an embodiment of the present invention, in step 4), the linear velocity of the blowing gas is generally 0.01-10 m/s (preferably 0.2-1 m/s). If the blowing gas velocity is too high, it will damage the dry-state filament precursor, destroying the fiber's mechanical strength or resulting in filament formation failure; whilst if it is too low, a sufficient pressure difference cannot be formed, and the ideal cross-section cannot be achieved.

[0083] According to an embodiment of the present invention, in step 4), stretching is optional, and the stretch ratio is generally 0-10 (preferably 3-5).

[0084] According to an embodiment of the present invention, the producing process further comprises step 5): after the end of step 4), cooling the as-spun monofilament at a temperature 1-120°C lower (preferably 30-50°C lower) than the melting point of the as-spun monofilament.

[0085] According to an embodiment of the present invention, in step 5), stretching is present or absent. If stretching is present, the stretch ratio is 1-10 (preferably 3-5).

[0086] According to a preferred embodiment of the present invention, during the entire process of producing the ultra-high molecular weight polyethylene monofilament or multifilament, no spinning finishing agent or similar agent is applied to the ultra-high molecular weight polyethylene monofilament or multifilament. As the said spinning finishing agent, specific examples include chemicals such as silicone oil, polyvinyl alcohol, polyacrylamide, etc., which have the effect of increasing cohesion. These agents generally contain oxygen atoms. These agents are not allowed in medical devices, especially medical devices implanted in the human body, which prevent the product from passing biocompatibility evaluation. The present invention does not use components other than ultra-high molecular weight polyethylene, ensuring sufficient purity of the fiber, and achieves bundling through self-locking embedded-interlocked of the monofilaments.

[0087] According to an embodiment of the present invention, it further relates to a medical product comprising the ultra-high molecular weight polyethylene monofilament according to any aspect of the present invention described above or below, the ultra-high molecular weight polyethylene multifilament according to any aspect of the present invention described above or below, or an ultra-high molecular weight polyethylene monofilament produced by the process according to any aspect of the present invention described above or below. The fiber of the present invention can be used without adding any other components, achieving improved cohesion through nesting between fiber monofilaments which not only maintains sufficient purity of the fiber but also gives the fiber good processability, and further eliminates manual treatment steps such as cleaning in the post-processing of the fiber.

[0088] According to the present invention, as the medical product, there may be mentioned at least one selected from the group consisting of medical supplies such as suture anchors for sports medicine repair, all-suture anchors, button plates with loops, high-strength webbings, high-strength non-absorbable sutures, cardiovascular repair balloons, spinal repair devices, ophthalmic repair sutures, artificial ligaments, and surgical sutures.

EXAMPLES

[0089] The following Examples and Comparative Examples further illustrate the present invention in detail, but the present invention is not limited to these Examples.

[0090] In the following Examples and Comparative Examples, unless otherwise specified, the number of short-chain branches per 1000 skeletal carbon atoms of the ultra-high molecular weight polyethylene was substantially 0.

Example 1

[0091] In this Example, an ultra-low solvent residue

ultra-high molecular weight polyethylene fiber was obtained by the following process:

Ultra-high molecular weight polyethylene and a solvent were mixed to prepare a spinning dope. The ultra-high molecular weight polyethylene had a viscosity-average molecular weight of 6,000,000. 100 parts by weight of ultra-high molecular weight polyethylene and 1300 parts by weight of the solvent were used. The solvent was decahydronaphthalene. The above components were mixed to prepare a spinning dope. The spinning dope was extruded through a spinneret equipped with 50 spinning orifices to form a spinning dope stream. The extrusion temperature was 175°C, the extrusion speed was 4 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 1 mm, the spinning orifices were arranged in an annular pattern on the spinneret, and the solvent content in the filament precursor was 92.9%.

[0092] After the spinning dope exited the spinneret holes, it was subjected to solvent removal and initial stretching at 200°C with a solvent concentration in the ambient atmosphere of 95.6%. The stretch ratio of the initial stretching was 4 for a duration of 10 s. After substantially completely removing the solvent from the spinning dope (to 300 ppm or less), a dry-state filament precursor was obtained. A blowing gas was provided from one side of the dry-state filament precursor at a temperature of 149°C, an angle of 90°, a linear velocity of 0.8 m/s, and a stretch ratio of 4, to obtain a high molecular weight polymer monofilament (called as as-spun monofilament).

[0093] The as-spun monofilament was cooled at 120°C and bundled to obtain an ultra-high molecular weight polyethylene multifilament, which was then subjected to multifilament stretching in 3 stages at a stretching temperature of 130°C and a total stretch ratio of 15.

[0094] An ultra-high molecular weight polyethylene fiber was finally obtained, which had a residual solvent content of 0.1 ppm, a surface carbon atom concentration of ≥99.8%, surface oxygen atom concentration being not detected, a polyethylene molecular chain entanglement degree of 3.5%, a monofilament fineness of 1.1 dtex, a fiber strength of 36 cN/dtex, a fiber modulus of 1506 cN/dtex, a linear density deviation of 5.8%, an inter-monofilament adhesion density of 0%, and a crystallinity of 77.8%. The cross-section had an average unfolded width of 25 μm, an average thickness of 5 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state.

[0095] The above fiber was useful as a braided thread for implantable grade suture anchors.

Example 2

[0096] Example 1 was repeated, except that the extrusion temperature was 180°C, the extrusion speed was 5 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 0.75 mm, the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 195°C with a solvent concentration in the ambient atmosphere of 96.8% for a duration of 16 s, and the solvent was substantially completely removed from the spinning dope (to 400 ppm or less).

[0097] The polyethylene molecular chain had an entanglement degree of 5.2%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 2 ppm, a surface carbon atom concentration of ≥99.6%, surface oxygen atom concentration being not detected, a monofilament fineness of 1.0 dtex, a fiber strength of 34 cN/dtex, a fiber modulus of 1324 cN/dtex, a linear density deviation of 6.0%, an inter-monofilament adhesion density of 0.6%, and a crystallinity of 75.0%. The cross-section had an average unfolded width of 36 μm, an average thickness of 6 μm, a ratio of central average thickness to end average thickness of 0.2, and in the multifilament, more than 88% of the total number of monofilaments were in an embedded-interlocked state.

[0098] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 3

[0099] Example 1 was repeated, except that the extrusion temperature was 170°C, the extrusion speed was 3 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 1.5 mm, the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 191°C with a solvent concentration in the ambient atmosphere of 90.2% for a duration of 60 s, and the solvent was substantially completely removed from the spinning dope (to 500 ppm or less). The polyethylene molecular chain had an entanglement degree of 10.3%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 10 ppm, a surface carbon atom concentration of ≥99.5%, surface oxygen atom concentration being not detected, a monofilament fineness of 1.9 dtex, a fiber strength of 30 cN/dtex, a fiber modulus of 1022 cN/dtex, a linear density deviation of 8.5%, an inter-monofilament adhesion density of 0.8%, and a crystallinity of 70.2%. The cross-section had an average unfolded width of 55 μm, an average thickness of 7 μm, a ratio of central average thickness to end average thickness of 0.5, and in the multifilament, more than 80% of the total number of monofilaments were in an embedded-interlocked state.

[0100] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 4

[0101] Example 1 was repeated, except that the extru-

sion temperature was 160°C, the extrusion speed was 2.2 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 1.9 mm, the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 189°C with a solvent concentration in the ambient atmosphere of 89.3% for a duration of 100 s, and the solvent was substantially completely removed from the spinning dope (to 600 ppm or less). The polyethylene molecular chain had an entanglement degree of 25%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 68 ppm, a surface carbon atom concentration of ≥98.2%, surface oxygen atom concentration being not detected, a monofilament fineness of 3.2 dtex, a fiber strength of 25 cN/dtex, a fiber modulus of 795 cN/dtex, a linear density deviation of 10.2%, an inter-monofilament adhesion density of 1.1%, and a crystallinity of 67%. The cross-section had an average unfolded width of 63 μm, an average thickness of 11 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 71% of the total number of monofilaments were in an embedded-interlocked state.

Example 5

[0102] Example 1 was repeated, except that the extrusion temperature was 150°C, the extrusion speed was 1.8 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 2.8 mm, the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 250°C with a solvent concentration in the ambient atmosphere of 88.5% for a duration of 3 s, and the solvent was substantially completely removed from the spinning dope (to 700 ppm or less). The polyethylene molecular chain had an entanglement degree of 0.5%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 150 ppm, a surface carbon atom concentration of ≥98.0%, surface oxygen atom concentration being not detected, a monofilament fineness of 4.0 dtex, a fiber strength of 20 cN/dtex, a fiber modulus of 762 cN/dtex, a linear density deviation of 11.0%, an inter-monofilament adhesion density of 5.2%, and a crystallinity of 61%. The cross-section had an average unfolded width of 71 μm, an average thickness of 15 μm, a ratio of central average thickness to end average thickness of 0.7, and in the multifilament, more than 65% of the total number of monofilaments were in an embedded-interlocked state.

Example 6

[0103] Example 1 was repeated, except that the extrusion temperature was 190°C, the extrusion speed was 8 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 0.45 mm, the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 189°C with a solvent concentration in the ambient atmosphere of 87.1% for a duration of 180 s, and the solvent was substantially completely removed from the spinning dope (to 1000 ppm or less). The polyethylene molecular chain had an entanglement degree of 32%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 382 ppm, a surface carbon atom concentration of ≥98.3%, surface oxygen atom concentration being not detected, a monofilament fineness of 1.1 dtex, a fiber strength of 19.4 cN/dtex, a fiber modulus of 751 cN/dtex, a linear density deviation of 11.0%, an inter-monofilament adhesion density of 2.0%, and a crystallinity of 57%. The cross-section had an average unfolded width of 48 μm, an average thickness of 4.1 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 62% of the total number of monofilaments were in an embedded-interlocked state.

Example 7

[0104] Example 1 was repeated, except that the extrusion temperature was 220°C, the extrusion speed was 18 m/min, the cross-sectional shape of the spinning orifices was circular with a diameter of 0.2 mm, the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 300°C with a solvent concentration in the ambient atmosphere of 85.2% for a duration of 0.3 s, and the solvent was substantially completely removed from the spinning dope (to 1000 ppm or less). An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 500 ppm, a polyethylene molecular chain entanglement degree of 0.8%, a surface carbon atom concentration of ≥98.0%, surface oxygen atom concentration being not detected, a monofilament fineness of 1.1 dtex, a fiber strength of 10.1 cN/dtex, a fiber modulus of 750 cN/dtex, a linear density deviation of 17.0%, an inter-monofilament adhesion density of 2.0%, and a crystallinity of 52%. The cross-section had an average unfolded width of 30 μm, an average thickness of 8 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 50% of the total number of monofilaments were in an embedded-interlocked state.

Example 8

[0105] Example 1 was repeated, except that the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 193°C with a solvent concentration in the ambient atmosphere of 95.2%, the stretch ratio of the initial stretching was 5 for a duration of 20 s, and the solvent was substantially completely removed from the spinning dope (to 1000 ppm or less); the blowing gas temperature was 145°C, the blowing angle was 80°, the linear velocity was 0.5 m/s, and the

stretch ratio was 5. The polyethylene molecular chain had an entanglement degree of 4.8%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 9 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.5 dtex, a fiber strength of 35 cN/dtex, a fiber modulus of 1473 cN/dtex, a linear density deviation of 3.5%, an inter-monofilament adhesion density of 0%, and a crystallinity of 76.2%. The cross-section had an average unfolded width of 35 μm, an average thickness of 5 μm, a ratio of central average thickness to end average thickness of 0.4, and in the multifilament, more than 92% of the total number of monofilaments were in an embedded-interlocked state.

[0106] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 9

[0107] Example 1 was repeated, except that the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 210°C with a solvent concentration in the ambient atmosphere of 95.5% for a duration of 12 s, and the solvent was substantially completely removed from the spinning dope (to 300 ppm or less); the stretch ratio of the initial stretching was 3, the blowing gas temperature was 142°C, the blowing angle was 85°, the linear velocity was 1.0 m/s, and the stretch ratio was 3. The polyethylene molecular chain had an entanglement degree of 6.2%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 8 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 2.1 dtex, a fiber strength of 34 cN/dtex, a fiber modulus of 1473 cN/dtex, a linear density deviation of 3.5%, an inter-monofilament adhesion density of 0.5%, and a crystallinity of 77.0%. The cross-section had an average unfolded width of 50 μm, an average thickness of 8 μm, a ratio of central average thickness to end average thickness of 0.3, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state.

[0108] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 10

[0109] Example 1 was repeated, except that the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 230°C with a solvent concentration in the ambient atmosphere of 95.5% for a duration of 9 s, and the solvent was substantially completely removed from the spinning dope (to 400 ppm or less); the stretch ratio of the initial stretching was 2, the blowing gas temperature was 138°C, the blowing angle was 70°, the linear velocity was 1.5 m/s, and the stretch ratio was 0. The polyethylene molecular chain had an entanglement degree of 7.2%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 98 ppm, a surface carbon atom concentration of ≥99.5%, surface oxygen atom concentration being not detected, a monofilament fineness of 2.2 dtex, a fiber strength of 28 cN/dtex, a fiber modulus of 970 cN/dtex, a linear density deviation of 10.5%, an inter-monofilament adhesion density of 2.4%, and a crystallinity of 67.0%. The cross-section had an average unfolded width of 53 μm, an average thickness of 9 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 75% of the total number of monofilaments were in an embedded-interlocked state.

Example 11

[0110] Example 1 was repeated, except that the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 186°C with a solvent concentration in the ambient atmosphere of 95.2% for a duration of 20 s, and the solvent was substantially completely removed from the spinning dope (to 500 ppm or less); the stretch ratio of the initial stretching was 8, the blowing gas temperature was 162°C, the blowing angle was 60°, the linear velocity was 0.1 m/s, and the stretch ratio was 7. The polyethylene molecular chain had an entanglement degree of 12%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 100 ppm, a surface carbon atom concentration of ≥98.0%, surface oxygen atom concentration being not detected, a monofilament fineness of 1.1 dtex, a fiber strength of 27 cN/dtex, a fiber modulus of 951 cN/dtex, a linear density deviation of 10.8%, an inter-monofilament adhesion density of 8.0%, and a crystallinity of 65%. The cross-section had an average unfolded width of 28 μm, an average thickness of 3.8 μm, a ratio of central average thickness to end average thickness of 0.8, and in the multifilament, more than 67% of the total number of monofilaments were in an embedded-interlocked state.

Example 12

[0111] Example 1 was repeated, except that the spinning dope, after exiting the spinneret hole, was subjected to the solvent removal and initial stretching at 230°C with a solvent concentration in the ambient atmosphere of 95.2% for a duration of 9 s, and the solvent was substantially completely removed from the spinning dope (to 600 ppm or less); the stretch ratio of the initial stretching was 2, the blowing gas temperature was 139°C, the blowing angle was 100°, the linear velocity was 10 m/s, and the stretch ratio was 8. The polyethylene molecular chain had an entanglement degree of 11.2%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 256 ppm,

a surface carbon atom concentration of ≥98.0%, surface oxygen atom concentration being not detected, a monofilament fineness of 3.5 dtex, a fiber strength of 22 cN/dtex, a fiber modulus of 880 cN/dtex, a linear density deviation of 12.1%, an inter-monofilament adhesion density of 2.0%, and a crystallinity of 60%. The cross-section had an average unfolded width of 71 μm, an average thickness of 12 μm, a ratio of central average thickness to end average thickness of 0.9, and in the multifilament, more than 52% of the total number of monofilaments were in an embedded-interlocked state.

Example 13

[0112] Example 1 was repeated, except that the stretch ratio of the initial stretching was 15. The polyethylene molecular chain had an entanglement degree of 4.7%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 325 ppm, a surface carbon atom concentration of ≥98.0%, surface oxygen atom concentration being not detected, a monofilament fineness of 0.75 dtex, a fiber strength of 12 cN/dtex, a fiber modulus of 770 cN/dtex, a linear density deviation of 15.1%, an inter-monofilament adhesion density of 6.2%, and a crystallinity of 65%. The cross-section had an average unfolded width of 15 μm, an average thickness of 10 μm, a ratio of central average thickness to end average thickness of 0.7, and in the multifilament, more than 42% of the total number of monofilaments were in an embedded-interlocked state.

Example 14

[0113] Example 9 was repeated , except that the blowing gas temperature was 110°C. The polyethylene molecular chain had an entanglement degree of 7.1%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 300 ppm, a surface carbon atom concentration of ≥98.0%, surface oxygen atom concentration being not detected, a monofilament fineness of 3.8 dtex, a fiber strength of 20 cN/dtex, a fiber modulus of 820 cN/dtex, a linear density deviation of 13.8%, an inter-monofilament adhesion density of 5.8%, and a crystallinity of 51%. The cross-section had an average unfolded width of 73 μm, an average thickness of 15 μm, a ratio of central average thickness to end average thickness of 0.9, and in the multifilament, more than 30% of the total number of monofilaments were in an embedded-interlocked state.

Example 15

[0114] Example 1 was repeated, except that the multifilament stretching was carried out in 2 stages at a stretching temperature of 120°C and a total stretch ratio of 10. The polyethylene molecular chain had an entanglement degree of 3.3%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 1.5 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.0 dtex, a fiber strength of 38 cN/dtex, a fiber modulus of 1580 cN/dtex, a linear density deviation of 2.4%, an inter-monofilament adhesion density of 0, and a crystallinity of 79.2%. The cross-section had an average unfolded width of 30 μm, an average thickness of 5 μm, a ratio of central average thickness to end average thickness of 0.2, and in the multifilament, more than 92% of the total number of monofilaments were in an embedded-interlocked state.

[0115] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 16

[0116] Example 1 was repeated, except that the multifilament stretching was carried out in 4 stages at a stretching temperature of 137°C and a total stretch ratio of 27. The polyethylene molecular chain had an entanglement degree of 3.6%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 0.5 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.0 dtex, a fiber strength of 37 cN/dtex, a fiber modulus of 1500 cN/dtex, a linear density deviation of 5.6%, an inter-monofilament adhesion density of 0, and a crystallinity of 78.1%. The cross-section had an average unfolded width of 38 μm, an average thickness of 5.5 μm, a ratio of central average thickness to end average thickness of 0.1, and in the multifilament, more than 95% of the total number of monofilaments were in an embedded-interlocked state.

[0117] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 17

[0118] Example 1 was repeated, except that the multifilament stretching was carried out in 5 stages at a stretching temperature of 140°C and a total stretch ratio of 30. The polyethylene molecular chain had an entanglement degree of 3.3%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 0.1 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.3 dtex, a fiber strength of 35 cN/dtex, a fiber modulus of 1418 cN/dtex, a linear density deviation of 6.0%, an inter-monofilament adhesion density of 0, and a crystallinity of 77.0%. The cross-section had an average unfolded width of 50 μm, an average thickness of 5.0 μm, a ratio of central average thickness to end average thickness of 0.1, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state.

[0119] The above fiber was useful as a braided thread and composite component for sports medicine devices.

Example 18

[0120] Example 1 was repeated, except that the multifilament stretching was carried out in 1 stage at a stretching temperature of 150°C and a total stretch ratio of 8. The polyethylene molecular chain had an entanglement degree of 4.0%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 100 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 3.1 dtex, a fiber strength of 20 cN/dtex, a fiber modulus of 763 cN/dtex, a linear density deviation of 17.5%, an inter-monofilament adhesion density of 1.7%, and a crystallinity of 65.0%. The cross-section had an average unfolded width of 65 μm, an average thickness of 12 μm, a ratio of central average thickness to end average thickness of 0.8, and in the multifilament, more than 60% of the total number of monofilaments were in an embedded-interlocked state.

Example 19

[0121] Example 1 was repeated, except that the multifilament stretching was carried out in 7 stages at a stretching temperature of 100°C and a total stretch ratio of 108. The polyethylene molecular chain had an entanglement degree of 5.2%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 2.0 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.0 dtex, a fiber strength of 25 cN/dtex, a fiber modulus of 802 cN/dtex, a linear density deviation of 11.3%, an inter-monofilament adhesion density of 13.5%, and a crystallinity of 60%. The cross-section had an average unfolded width of 25 μm, an average thickness of 3 μm, a ratio of central average thickness to end average thickness of 0.8, and in the multifilament, more than 58% of the total number of monofilaments were in an embedded-interlocked state.

Example 20

[0122] Example 1 was repeated, except that no multifilament stretching was performed. The polyethylene molecular chain had an entanglement degree of 13%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 698 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 5.6 dtex, a fiber strength of 4.2 cN/dtex, a fiber modulus of 502 cN/dtex, a linear density deviation of 18.3%, an inter-monofilament adhesion density of 36.2%, and a crystallinity of 35%. The cross-section had an average unfolded width of 125 μm, an average thickness of 22 μm, a ratio of central average thickness to end average thickness of 0.8, and in the multifilament, more than 18% of the total number of monofilaments were in an embedded-interlocked state.

Example 21

[0123] Example 1 was repeated, except that no stretching was performed during the blowing gas blowing to the dry-state filament precursor. The polyethylene molecular chain had an entanglement degree of 15%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 10 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.2 dtex, a fiber strength of 35 cN/dtex, a fiber modulus of 1402 cN/dtex, a linear density deviation of 3.5%, an inter-monofilament adhesion density of 0.5%, and a crystallinity of 77.3%. The cross-section had an average unfolded width of 45 μm, an average thickness of 6.5 μm, a ratio of central average thickness to end average thickness of 0.8, and in the multifilament, more than 92% of the total number of monofilaments were in an embedded-interlocked state.

Example 22

[0124] Example 1 was repeated, except that the spinneret orifices had a flat arc shape. The polyethylene molecular chain had an entanglement degree of 4.6%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 295 ppm, a surface carbon atom concentration of ≥99.8%,a monofilament fineness of 1.5 dtex, surface oxygen atom concentration being not detected, a fiber strength of 18.5 cN/dtex, a fiber modulus of 759 cN/dtex, a linear density deviation of 13.2%, an inter-monofilament adhesion density of 2.1%, and a crystallinity of 56.3%. The cross-section had an average unfolded width of 110 μm, an average thickness of 2.1 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 35% of the total number of monofilaments were in an embedded-interlocked state.

Example 23

[0125] Example 1 was repeated, except that the blowing gas was provided from both sides. The polyethylene molecular chain had an entanglement degree of 3.6%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 5.6 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.5 dtex, a fiber strength of 33.8 cN/dtex, a fiber modulus of 1210 cN/dtex, a linear density deviation of 6.7%, an inter-monofilament adhesion density of 0.8%, and a crystallinity of 65.6%. The cross-section was nearly dumbbell-shaped, and

65% of the monofilaments in the multifilament were in an embedded-interlocked state.

Example 24

[0126] Example 1 was repeated, except that the blowing gas was provided from the circumferential direction. The polyethylene molecular chain had an entanglement degree of 6.8%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 4.6 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.5 dtex, a fiber strength of 34.2 cN/dtex, a fiber modulus of 1305 cN/dtex, a linear density deviation of 5.0%, an inter-monofilament adhesion density of 0.5%, and a crystallinity of 67.1%. The cross-section was nearly dumbbell-shaped, and 68% of the monofilaments in the multifilament were in an embedded-interlocked state.

Example 25

[0127] Example 1 was repeated, except that the raw material was ultra-high molecular weight polyethylene having a short-chain branch content of 15.0/1000C. The final polyethylene molecular chain entanglement degree was 7.3%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 0.2 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.1 dtex, a fiber strength of 40 cN/dtex, a fiber modulus of 1735 cN/dtex, a linear density deviation of 2.2%, an inter-monofilament adhesion density of 0%, and a crystallinity of 78.3%. The cross-section had an average unfolded width of 25 μm, an average thickness of 5 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state. The fiber had a creep elongation rate of 3.5%.

[0128] The above fiber was useful as a braided thread for implantable grade suture anchors.

Example 26

[0129] Example 1 was repeated, except that the raw material was ultra-high molecular weight polyethylene having a short-chain branch content of 50.0/1000C. The final polyethylene molecular chain entanglement degree was 32%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 2 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a monofilament fineness of 1.1 dtex, a fiber strength of 26 cN/dtex, a fiber modulus of 842 cN/dtex, a linear density deviation of 7.2%, an inter-monofilament adhesion density of 0.9%, and a crystallinity of 55.8%. The cross-section had an average unfolded width of 25 μm, an average thickness of 5 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state. The fiber had a creep elongation rate of 2.0%.

Example 27

[0130] Example 1 was repeated, except that the raw material was ultra-high molecular weight polyethylene having a short-chain branch content of 200/1000C. Finally, the raw material could not be well disentangled and spinning failed.

Example 28

[0131] Example 1 was repeated, except that 100 parts by weight of ultra-high molecular weight polyethylene, 1300 parts by weight of the solvent, and 1.8 parts by weight of cobalt chrome blue pigment were used.

[0132] The final polyethylene molecular chain entanglement degree was 3.3%. A light blue ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 0.4 ppm, a monofilament fineness of 1.2 dtex, a fiber strength of 32 cN/dtex, a fiber modulus of 1250 cN/dtex, a linear density deviation of 4.0%, an inter-monofilament adhesion density of 0%, and a crystallinity of 70.5%. The cross-section had an average unfolded width of 25 μm, an average thickness of 6 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state. The fiber had a color hue of L75.93, with a-14.35, and b-14.51.

[0133] The above fiber was useful as an implantable medical braided thread.

Example 29

[0134] Example 1 was repeated, except that 100 parts by weight of ultra-high molecular weight polyethylene, 1300 parts by weight of the solvent, and 1.5 parts by weight of chromium oxide pigment were used.

[0135] The final polyethylene molecular chain entanglement degree was 3.1%. A light green ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 0.4 ppm, a monofilament fineness of 1.2 dtex, a fiber strength of 33 cN/dtex, a fiber modulus of 1128 cN/dtex, a linear density deviation of 4.1 %, an inter-monofilament adhesion density of 0%, and a crystallinity of 70.9%. The cross-section had an average unfolded width of 25 μm, an average thickness of 7 μm, a ratio of central average thickness to end average thickness of 0.5, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state. The fiber had a color hue of L78.10, with a-16.71, and b 10.30.

[0136] The above fiber was useful as an implantable medical braided thread.

Example 30

[0137] Example 1 was repeated, except that 100 parts by weight of ultra-high molecular weight polyethylene, 1300 parts by weight of the solvent, and 1.0 part by weight of carbon black pigment were used.

[0138] The final polyethylene molecular chain entanglement degree was 4.7%. A black ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 0.4 ppm, a monofilament fineness of 1.2 dtex, a fiber strength of 35 cN/dtex, a fiber modulus of 1403 cN/dtex, a linear density deviation of 3.5%, an inter-monofilament adhesion density of 0%, and a crystallinity of 71.3%. The cross-section had an average unfolded width of 24 μm, an average thickness of 7 μm, a ratio of central average thickness to end average thickness of 0.5, and in the multifilament, more than 90% of the total number of monofilaments were in an embedded-interlocked state. The fiber had a color hue of L 30.21, with a 0.43, and b 1.72.

[0139] The above fiber was useful as an implantable medical braided thread.

Example 31

[0140] Example 1 was repeated, except that the solvent removal and initial stretching were performed under an ambient atmosphere with a solvent concentration of 50% after the spinning dope exited the spinneret holes, and the solvent was substantially completely removed from the spinning dope (to 1000 ppm or less). An ultra-high molecular weight polyethylene fiber was finally obtained, which had a residual solvent content of 482 ppm, a surface carbon atom concentration of ≥99.8%, surface oxygen atom concentration being not detected, a polyethylene molecular chain entanglement degree of 3.5%, a monofilament fineness of 1.5 dtex, a fiber strength of 12.5 cN/dtex, a fiber modulus of 701 cN/dtex, a linear density deviation of 13.5%, an inter-monofilament adhesion density of 2.3%, and a crystallinity of 52.3%. The cross-section had an average unfolded width of 116 μm, an average thickness of 2.3 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 35% of the total number of monofilaments were in an embedded-interlocked state.

Example 32

[0141] Example 1 was repeated, except that the solvent removal and initial stretching were performed under an ambient atmosphere with a solvent concentration of 80% after the spinning dope exited the spinneret holes, and the solvent was substantially completely removed from the spinning dope (to 400 ppm or less). An ultra-high molecular weight polyethylene fiber was finally obtained, which had a residual solvent content of 82 ppm, a surface carbon atom concentration of ≥99.8%, surface oxygen atom concentration being not detected, a polyethylene molecular chain entanglement degree of 3.2%, a monofilament fineness of 1.1 dtex, a fiber strength of 28.2 cN/dtex, a fiber modulus of 975 cN/dtex, a linear density deviation of 12.1%, an inter-monofilament adhesion density of 2.2%, and a crystallinity of 56.3%. The cross-section had an average unfolded width of 118 μm, an average thickness of 2.3 μm, a ratio of central average thickness to end average thickness of 0.6, and in the multifilament, more than 45% of the total number of monofilaments were in an embedded-interlocked state.

Example 33

[0142] Example 1 was repeated, except that there was no wind-shaping zone. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 218 ppm, a nearly circular cross-section, and almost no cohesion.

Example 34

[0143] Example 1 was repeated, except that the spinning dope stream was not stretched when passing through the solvent removal zone. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 490 ppm.

Example 35

[0144] Example 1 was repeated, except that the spinning dope stream was not passed through the solvent removal zone. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 500 ppm, and a nearly circular cross-section, without interlocking state.

Comparative Example 1

[0145] Example 1 was repeated, except that the solvent removal and initial stretching were performed under an ambient atmosphere with a solvent concentration of 45% after the spinning dope exited the spinneret holes, and the solvent was substantially completely removed from the spinning dope (to 1500 ppm or less). An ultra-high molecular weight polyethylene fiber was finally obtained, which had a residual solvent content of 682 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a polyethylene molecular chain entanglement degree of 3.2%, a monofilament fineness of 1.1 dtex, a fiber strength of 4.1 cN/dtex, a fiber modulus of 328 cN/dtex, a linear density deviation of 15.1%, an inter-monofilament adhesion density of 2.2%, and a crystallinity of 30.5%. The cross-section had an average unfolded width of 118 μm, an average thickness of 2.3 μm, a ratio of central average

thickness to end average thickness of 0.6, and in the multifilament, almost no monofilaments were in an embedded-interlocked state.

Comparative Example 2

[0146] Example 1 was repeated, except that the solvent removal and initial stretching were performed under an ambient atmosphere with a solvent concentration of 30% after the spinning dope exited the spinneret holes, and the solvent was substantially completely removed from the spinning dope (to 2000 ppm or less). An ultra-high molecular weight polyethylene fiber was finally obtained, which had a residual solvent content of 709 ppm, a surface carbon atom concentration of ≥99.8%,surface oxygen atom concentration being not detected, a polyethylene molecular chain entanglement degree of 3.2%, a monofilament fineness of 1.1 dtex, a fiber strength of 3.1 cN/dtex, a fiber modulus of 228 cN/dtex, a linear density deviation of 15.6%, an inter-monofilament adhesion density of 2.2%, and a crystallinity of 29.1%. The monofilament shell layer was broken, without embedded-interlocked state.

Comparative Example 3

[0147] Example 1 was repeated, except that the solvent removal and initial stretching were performed under an ambient atmosphere with a solvent concentration of 20% after the spinning dope exited the spinneret holes. A shell layer formed rapidly, and normal spinning could not be carried out.

Comparative Example 4

[0148] Example 1 was repeated, except that the ambient temperature after the spinning dope exited the spinneret holes was room temperature. The fiber could not be normally formed into filaments.

Comparative Example 5

[0149] Example 1 was repeated, except that after the spinning dope stream passed through the solvent removal zone, the solvent residue was 4000 ppm or more. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 2180 ppm.

Comparative Example 6

[0150] This Comparative Example followed a gel process of the prior art. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 602 ppm, a nearly circular cross-section, and almost no cohesion.

Comparative Example 7

[0151] Example 1 was repeated, except that the solvent removal and initial stretching were performed at 170°C (solvent concentration of 35%) after the spinning dope exited the spinneret holes, for which the duration was 185 s, and the solvent removal was slow.

Comparative Example 8

[0152] Example 1 was repeated, except that the blowing gas was provided immediately after the spinning dope exited the spinneret, and the solvent concentration was 93%. The polyethylene molecular chain had an entanglement degree of 1%. An ultra-high molecular weight polyethylene fiber was obtained, which had a residual solvent content of 603 ppm, a surface carbon atom concentration of ≥99.8%, surface oxygen atom concentration being not detected, a monofilament fineness of 1.8 dtex, a fiber strength of 4.8 cN/dtex, a fiber modulus of 545 cN/dtex, a linear density deviation of 23%, an inter-monofilament adhesion density of 42.6%, and a crystallinity of 35.1%. The cross-section had an average unfolded width of 150 μm, an average thickness of 2.5 μm, a ratio of central average thickness to end average thickness of 0.8, and in the multifilament, more than 38% of the total number of monofilaments were in an embedded-interlocked state.

Claims

1. A process for producing a high molecular weight polymer monofilament (particularly an ultra-high molecular weight polyethylene monofilament), comprising subjecting a filament precursor (particularly a spinning dope stream) comprising a high molecular weight polymer (such as an ultra-high molecular weight polyethylene) and a solvent (such as decahydronaphthalene) to an ambient atmosphere as follows: the ambient atmosphere has an elevated temperature (called as ambient temperature), and the concentration of the solvent in the ambient atmosphere is 50 vol% or more (preferably 80 vol% or more, 85 vol% or more, 90 vol% or more, or 95 vol% or more), based on the total volume of the ambient atmosphere as 100 vol%.

2. The process according to claim 1, wherein the ambient temperature is higher than the boiling point of the solvent (preferably 0.1-150°C, 0.2-100°C, 0.4-50°C, 0.5-20°C, 0.5-10°C, or 0.5-5°C higher than the boiling point of the solvent).

3. The producing process according to claim 1, wherein the subjecting is carried out in a hollow cylinder, the hollow cylinder comprises a top opening, a bottom opening, and a side wall (i.e. shell) connecting the top opening with the bottom opening and formed

around the central axis of the hollow cylinder, the filament precursor leaves the hollow cylinder through the bottom opening, and a heating member is provided on at least a part of the side wall to make the temperature of the inner cavity of the hollow cylinder to reach the ambient temperature.

4. The producing process according to claim 1, wherein no or substantially no diluent gas is proactively introduced into the ambient atmosphere.

5. The producing process according to claim 1, wherein the ultra-high molecular weight polyethylene has a short-chain branch content of 3-100 (preferably 3-30) short-chain branches per 1000 skeletal carbon atoms.

6. The producing process according to claim 1, wherein the solvent is removed from the filament precursor in the ambient atmosphere until the solvent content in the filament precursor reaches 1000 ppm or less (preferably 500 ppm or less, 100 ppm or less, 50 ppm or less, or 10 ppm or less).

7. The producing process according to claim 1, wherein the filament precursor is stretched while subjected to the ambient atmosphere, called as initial stretching.

8. The producing process according to claim 7, wherein the initial stretching causes the cross-sectional shrinkage ratio of the filament precursor to reach 10-10^6 (preferably 100-1000).

9. The producing process according to claim 7, wherein the stretch ratio of the initial stretching is 1-10 (preferably 3-5).

10. The producing process according to claim 1, wherein the duration of the subjecting is 0.5-180 s (preferably 5-60 s).

11. The producing process according to claim 1, wherein the solvent content in the filament precursor is 80-97 wt% (preferably 90-95 wt%), based on the total weight of the filament precursor as 100 wt%.

12. The producing process according to claim 1, wherein the solvent is decahydronaphthalene, and the ambient temperature is 189-320°C (preferably 191-210°C).

13. The producing process according to claim 1, comprising the steps of:

1) mixing the high molecular weight polymer with the solvent to prepare a spinning dope,
2) extruding the spinning dope through a spinneret to form the filament precursor,
3) stretching the filament precursor under the ambient atmosphere, called as initial stretching, to obtain a dry-state filament precursor.

14. The producing process according to claim 13, further comprising step of:
4) providing a blowing gas to the dry-state filament precursor, with or without stretching, to obtain an as-spun monofilament.

15. The producing process according to claim 14, wherein through the blowing, the solvent content in the filament precursor reaches 100 ppm or less (preferably 50 ppm or less, 10 ppm or less, 5 ppm or less, 2 ppm or less, or 1 ppm or less).

16. The producing process according to claim 14, wherein in step 4), the blowing gas is provided to the dry-state filament precursor only from one side of the dry-state filament precursor.

17. The producing process according to claim 14, wherein in step 4), the temperature of the blowing gas is 0-50°C higher (preferably 1-10°C higher) than the melting point of the dry-state filament precursor, or the temperature of the blowing gas is ≥138°C (preferably 140-150°C), and the linear velocity of the blowing gas is 0.01-10 m/s (preferably 0.2-1 m/s).

18. The producing process according to claim 14, wherein in step 4), the stretch ratio is 0-10 (preferably 3 to 5).

19. An ultra-high molecular weight polyethylene monofilament, having a polyethylene molecular chain entanglement degree of 0%-50% (preferably 1%-20%), and a spinning solvent content of 500 ppm or less (preferably 100 ppm or less, 50 ppm or less, 10 ppm or less, or 1 ppm or less), relative to the total weight of the ultra-high molecular weight polyethylene monofilament as 100 wt%.

20. The ultra-high molecular weight polyethylene monofilament according to claim 19, having a monofilament fineness of 0.5-10 dtex (preferably 0.55-3.0 dtex), and/or a fiber strength of 5-50 cN/dtex (preferably 30-45 cN/dtex), and/or a fiber modulus of ≥750 cN/dtex (preferably 800-1800 cN/dtex), and/or a linear density deviation of ≤20% (preferably ≤10%).

21. The ultra-high molecular weight polyethylene monofilament according to claim 19, having a crystallinity of ≥50% (preferably ≥70%), and/or an inter-monofilament adhesion density of ≤100% (preferably ≤50%, preferably ≤10%, preferably ≤1%), and/or a surface carbon atom concentration of 98% or more (preferably 99% or more, 99.5% or more, or substantially 100%), and a surface oxygen atom con-

centration of 2% or less (preferably 1% or less, 0.5% or less, or not detected), wherein each surface atomic concentration is measured by XPS analysis.

22. The ultra-high molecular weight polyethylene monofilament according to claim 19, having a cross-section in a free state of a flat and elongated arc shape, wherein the cross-section has an average unfolded width of 10 μm or more (preferably 15-100 μm or 20-60 μm), and the cross-section has an average thickness of 2 μm or more (preferably 3-20 μm or 5-10 μm).

23. The ultra-high molecular weight polyethylene monofilament according to claim 19, wherein a ratio of the average unfolded width of the cross-section to the average thickness of the cross-section is 2 or more (preferably 3-100 or 4-20), and a ratio of the central average thickness to the end average thickness of the cross-section is less than 1 (preferably ≤0.7).

24. The ultra-high molecular weight polyethylene monofilament according to claim 19, which does not comprise a spinning finishing agent or any residue derived therefrom.

25. The ultra-high molecular weight polyethylene monofilament according to claim 19, having a creep elongation rate of ≤10% (preferably ≤5%).

26. The ultra-high molecular weight polyethylene monofilament according to claim 19, which can be produced by the process according to any one of claims 1-18.

27. An ultra-high molecular weight polyethylene multifilament, formed by bundling a plurality of (e.g., 2-10000, preferably 5-400) the ultra-high molecular weight polyethylene monofilaments according to any one of claims 19-26 or the ultra-high molecular weight polyethylene monofilaments produced by the process according to any one of claims 1-18, wherein in the ultra-high molecular weight polyethylene multifilament, 50% or more (preferably 60% or more, 70% or more, 80% or more, or 90% or more) of the total number of the ultra-high molecular weight polyethylene monofilaments are in an embedded-interlocked state.

28. A medical product, comprising the ultra-high molecular weight polyethylene monofilament according to any one of claims 19-26, the ultra-high molecular weight polyethylene multifilament according to claim 27, or an ultra-high molecular weight polyethylene monofilament produced by the process according to any one of claims 1-18.

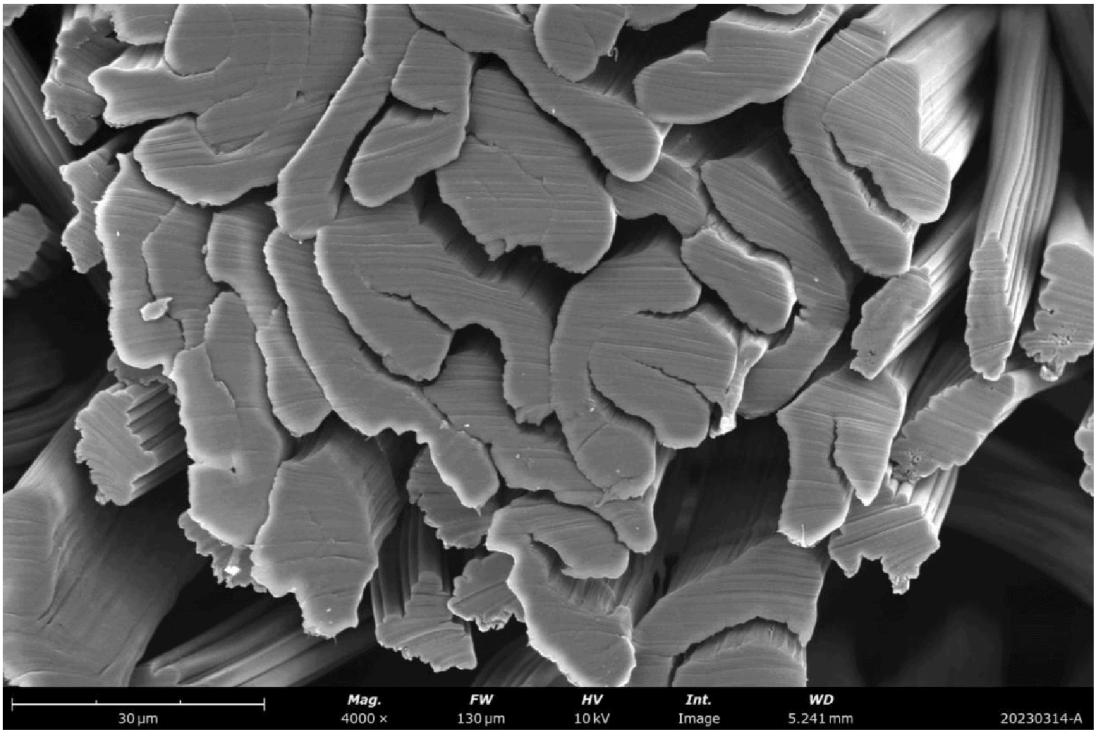

30 µm
Mag.
4000 ×
FW
130 µm
HV
10 kV
Int.
Image
WD
5.241 mm
20230314-A

Fig. 1

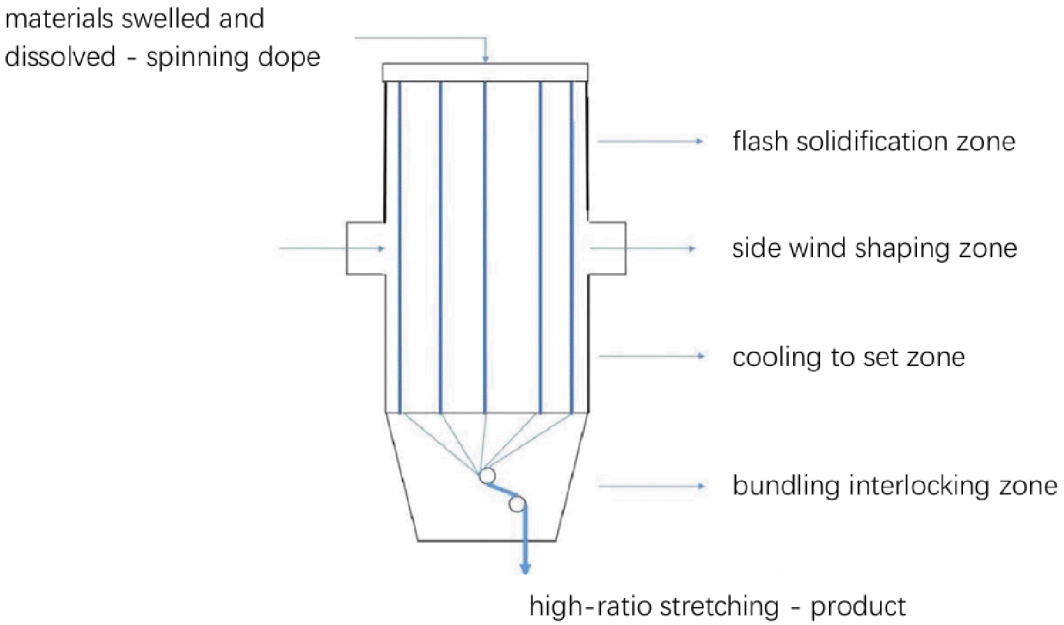

materials swelled and dissolved - spinning dope
flash solidification zone
side wind shaping zone
cooling to set zone
bundling interlocking zone
high-ratio stretching - product

Fig. 2

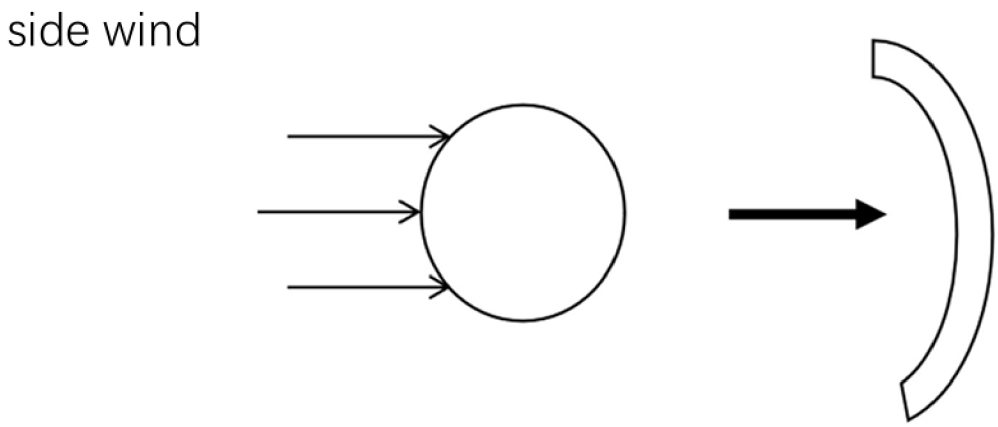


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2024/134396

A. CLASSIFICATION OF SUBJECT MATTER

D01D5/04(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC:D01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNTXT, ENTXTC, JPTXT, VEN, WPABSC: 抱合, 残留, 侧吹, 缠结度, 聚乙烯, 复丝, 烘箱, 弧形, 环境, 溶剂, 蒸气, 丝, 医, PE, PPM, UHMWPE, residual, side, entanglement, polyethylene, multifilament, oven, arc, filament, medical

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 113718360 A (JIESHOU SAMBO HONDAR THREAD CO., LTD.) 30 November 2021 (2021-11-30) description, specific embodiments, and figures 1-6	1-16, 18, 28
Y	CN 113718360 A (JIESHOU SAMBO HONDAR THREAD CO., LTD.) 30 November 2021 (2021-11-30) description, specific embodiments, and figures 1-6	26
X	CN 101646811 A (DSM IP ASSETS B.V.) 10 February 2010 (2010-02-10) description, page 6, paragraph 2	19-21, 24-25, 28
Y	CN 101646811 A (DSM IP ASSETS B.V.) 10 February 2010 (2010-02-10) description, page 6, paragraph 2	26
A	CII 143345 A (WACKER CIIEMIE GMBII) 15 November 1930 (1930-11-15) entire document	1-28
A	CN 101137777 A (HONEYWELL INTERNATIONAL INC.) 05 March 2008 (2008-03-05) entire document	1-28

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 January 2025	**22 January 2025**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2024/134396

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 104032402 A (CHINA TEXTILE ACADEMY) 10 September 2014 (2014-09-10) entire document	1-28
A	CN 108166087 A (WANG HUILI) 15 June 2018 (2018-06-15) entire document	1-28
A	CN 111254511 A (SHANGHAI RESEARCH INSTITUTE OF CHEMICAL INDUSTRY CO., LTD.) 09 June 2020 (2020-06-09) entire document	1-28

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2024/134396

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 113718360 A	30 November 2021	None	
CN 101646811 A	10 February 2010	JP 2010522286 A	01 July 2010
		US 2010086781 A1	08 April 2010
		WO 2008116613 A1	02 October 2008
		JP 2014129638 A	10 July 2014
		EP 2126167 A1	02 December 2009
		US 2016201225 A1	14 July 2016
CH 143345 A	15 November 1930	None	
CN 101137777 A	05 March 2008	WO 2006073743 A1	13 July 2006
		USRE 41268 E	27 April 2010
		KR 20070094948 A	27 September 2007
		US 2006267229 A1	30 November 2006
		EP 1841906 A1	10 October 2007
		US 7147807 B2	12 December 2006
		JP 4840784 B2	21 December 2011
CN 104032402 A	10 September 2014	None	
CN 108166087 A	15 June 2018	None	
CN 111254511 A	09 June 2020	None	

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- GB T19975 A **[0019]**
- GB T14343 A **[0020]**
- GB T416712022 A **[0023]**
- GB T39162013 A **[0024]**
- GB T199752005 A **[0025]**