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# (54) A PROCESS FOR PRODUCING FIBER OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

(57) A process for producing fiber of ultra high molecular weight polyethylene, with a flat cross-section and high cohesiveness, is disclosed. The process includes: distributing the powder of UHMWPE into a solvent evenly; preparing an uniform emulsion mixture by properly untangling with high shear; at the same time adding polar polymer comprising polar groups, for example a carboxyl group, a carbonyl group, an ether group, or an ester group and so on; evenly distributing the polar polymer together with the polyethylene powder in the solvent to form an uniform emulsion mixture; forming a gel filament from the emulsion mixture by gel spinning method, then extracting, drying, and stretching so as to obtain the UHMWPE fiber, with a flat cross section, high strength and cohesiveness. By properly untangling, the swelling and dissolving of the ultra high molecular weight polyethylene can be accelerated, while the polar polymer being evenly distributed therein can significantly improve the adhesive property of the fiber. The operations in the production method are easy, and furthermore, time, labor and cost can be saved. The section of the fiber is of a flat rectangle shape and the wall is thin and even, so the path for the solvent in the fiber diffusing out of the gel filament can be significantly shorten, and thus the efficiency of extraction and the uniformity of the fiber can be improved.

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## Description

### FIELD OF THE INVENTION

**[0001]** The invention relates to a method of preparing fiber of High Molecular Weight Polyethylene (HMWPE), specifically, a method of preparing fiber of Ultra High Molecular Weight Polyethylene (UHMWPE).

### BACKGROUND OF THE INVENTION

**[0002]** A method of preparing a high strength, high modulus polyethylene (PE) fiber from UHMWPE gel *via* drawing or stretching technology is disclosed in UK Patent Nos. GB2042414 and GB2051667, assigned to DSM Company, Netherlands in 1979. After that, this technology was industrialized by Allied Company from the U.S., Toyobo-DSM Company, a joint venture by Japan and Netherlands, as well as Mitsui Company from Japan. In 1982, Allied Company obtained US Patent No. 4413110, which covers a process of preparing UHMWPE fiber. Donghua University in China also obtained Chinese Patent Nos. 89107905 and 97106768 in this area.

**[0003]** The main procedures for preparing UHMWPE gel fiber are as follows: UHMWPE is added into a suitable solvent to prepare a solution by stirring; the solution is extruded by an extruder and spun through a spinnerette, followed by cooling, extraction, drying, and stretching, to form the desired fiber product. To obtain a high strength and high modulus fiber, key steps include the preparation of a homogeneous UHMWPE solution, and the extraction with a second solvent to remove the large amount of a first solvent contained in gel fiber prior to stretching of the gel fiber.

**[0004]** As the molecular weight of polyethylene increases, its macromolecular size is also increasing, and the entanglement exists among such macromolecules. The entanglement among the macromolecules is beneficial to increase the draw ratio and can result in highly oriented fiber with higher strength and modulus. However, the viscoelastic effect due to the entanglement among the macromolecules of polymer makes the dissolving process much more complicated, and is not beneficial to the dissolving and shaping process. Therefore, the entanglement among the macromolecules should be controlled. The state of such entanglement can be controlled by heat treatment, solvent treatment and cutting.

**[0005]** The molecular weight for polymer and low molecule solvent is quite different. Polymer has a long molecule chain and it is difficult for the polymer to move. Due to the strong intra-molecular interactions and entanglement among the polymer molecules, the polymer does not diffuse into a solvent when the polymer and low molecule solvent are just mixed. If the conventional dissolution method is used to prepare the solution, the polymer powder tends to be aggregated, or form a gel solid due to incomplete permeation of the solvent, and a homogeneous solution cannot be obtained. Furthermore, the Weissenberg Effect (climbing effect) will appear due to the viscoelastic effect caused by entanglement between macromolecules of polyethylene when stirring.

**[0006]** With the increase of molecule weight, polymer concentration and stirring speed, the Weissenberg Effect will be more effective. Accordingly, it will become more difficult to obtain a homogeneous solution.

**[0007]** Certain patents propose various methods for solving the problem. For example, EP 0255618 discloses that a hydrocarbon mixture free of naphthalin and diphenyl, with boiling point around 180-250°C is obtained after a rectification separation from hydrogenated coal oil. Such hydrocarbon mixture is further mixed with UHMWPE and decahydronaphthalene at 135°C, agitated for several hours to form a PE solution. The concentration of the PE solution is no greater than 50%.

**[0008]** Japanese Patent No. 59232123 describes a process to mix UHMWPE with small amount of a solvent for several minutes, followed by heating, then more solvent is added gradually with stirring to form a solution containing UHMWPE.

**[0009]** In an example disclosed in Japanese Patent No. 63-15838, a fractional coal oil is catalytically hydrogenated to provide a solvent. The solvent is further added with an anti-oxidant and PE, and the resulting mixture is agitated for 3 hours at 140°C to form a 10%(w/w) UHMWPE solution.

**[0010]** In some cases, the problem is solved using a two-step process including swelling and dissolving. Chinese Patent No. 970106768 discloses that an alkane hydrocarbon solvent can be used to swell PE under certain conditions, and to prepare a suspension solution containing UHMWPE.

**[0011]** Chinese Patent No. 97101010 describes that a pre-swelling pan equipped with an new mixer baffle is used to swell UHMWPE to form a suspension solution so as to avoid the Weissenberg Effect of UHMWPE during dissolving and stirring.

**[0012]** Chinese Patent No. 20041009607615, titled "A Method For Continuous Mixing and Preparation of UHMWPE Solution," discloses the use of a static mixer with a screw having a small Length/Diameter ratio to allow continuous preparation of UHMWPE solution. In Chinese Patent No. 85107352A, DSM company provides a method of preparing a homogeneous solution of polymer, comprising: feeding a fine polymer powder and a solvent into an extruder, where a suspension and a solution is formed within the extruder, with an operation temperature above the melting point of the polymer and at a mechanical cutting rate of about 30-2000$S^{-1}$. However, this method can damage the molecule chain of UHMWPE and result in a decrease of its molecular weight.

**[0013]** Although the patents mentioned above made certain improvements on the process related to solvent and dissolving, the following problems still exist: the processing equipment is complicated; the process is not stable. In addition, there is a safety risk associated with the process, and the tenacity of so obtained fiber is decreased.

**[0014]** The fiber with high strength and high modulus can be obtained only after large amount of the first solvent contained in the gel fiber is extracted with a second solvent and the stretching of the gel fiber is performed. The extraction speed depends on the second solvent used, the extraction process, as well as the diffusion path of the solvent. During the course of the extraction, the solvent in the outer surface of the fiber will first diffuse from the gel fiber. The longer the diffusion distance, the bigger the difference in diffusion speeds. According to the current method, the cross section of a PE gel fiber is round and has a thicker wall. The bigger the difference, the easier to form a skin-core structure, which is not a homogeneous structure and which has a negative influence on the stretching process so as to affect the mechanical properties of the fiber product.

**[0015]** Currently, there are some patents related to the preparing of profiled HDPE fiber membrane, including US Patent Nos. 4115492, 5294338, 6436319 and ZL200510049263, all of which use melting spinning; and US Patent No. 5695702 and ZL95193838, which use thermoplastic hollow fiber membrane module and method of manufacture. The methods described therein above suffer the problem of high cost, while the homogeneity of the fiber structure obtained is not satisfying.

**[0016]** Furthermore, the preparation of high strength and high modulus PE fiber by stretching or drawing UHMWPE gel fiber has already been industrialized. The searched patents for PE gel fiber include EP 0205960A, EP 0213208A1, US Patent No. 4413110, WO 01/73173A1, and EP 1746187A1, which made some modifications on spinning technology. For the UHMWPE gel spinning process, it is critical to obtain a homogeneous polymer solution and a stable drawing of gel fiber. As a pre-condition for the formation of fiber with stable properties, it is important to have a good solution and a stable drawing operation.

**[0017]** Because PE fiber has the advantages of light weight, flexible, high strength and high modulus, UV-proof, anti-impact, and anti-corrosion to seawater, it can be used for cutting-proof gloves, bullet-proof jacket or helmet, cable etc. In most circumstances, one kind or several kinds of base materials, such as acrylonitrile butadiene rubber, polyurethane and epoxy resin, can be combined with the PE fiber. Due to the inertia surface of the PE fiber, the interface adhesion between the fiber and the base material is poor, which has brought great attention of those skilled in this field. To improve the interface adhesion strength between the fiber and the base resin, certain methods of surface treatment, including surface grafting improving, chemical agent etching, plasma processing, corona arc treatment, and photo-oxidation surface modification, etc., have been used to activate the inertia surface of the PE fiber.

**[0018]** US Patent No. 480136 discloses that during spinning, thermal initiated surface silanization grafting reaction occurs on PE fiber, with a further cross-linking process, and results in the improvement of the adhesive property of the PE fiber. However, the process has a negative influence on the subsequent drawing process, and the mechanical properties of the fiber is not satisfying. US 5039549, US 5755913 and ZL03115300.3 describe that plasma, ozone, corona arc or UV radiation can be used to improve the adhesive property on PE fiber surface. However, these processes are complicated and involve expensive equipment, and the process parameters are difficult to control. Therefore, the processes are difficult to be industrialized.

**[0019]** Jiang Shen et al. proposes to use strong oxidizing agents, such as chromic acid, kali permanganate, to etch the surface of the PE fiber (see, UHMWPE Fiber Adhesive Property Study, Reinforced Glass/Complex Material, 2004 (3):47). Because this method requires the merging of the PE fiber in a strong oxidation environment for a long time, while the fiber infiltrating property may be improved, the mechanical properties of the fiber is decreased. In addition, such processes are also complicated, with a strict requirement on the equipment, and also have the pollution problem from the waste liquid.

**[0020]** CN163544 proposes to use a composite extracting agent containing polar polymer compound to treat the spinned PE gel fiber to improve the adhesive property on the fiber surface while maximally maintaining the original strength of the fiber. This process is relatively simple, without requiring any additional equipment. Although this process is efficient for loose gel fiber, in practical production with tension extraction, it is difficult for polar polymer compound to diffuse into gel fiber, and therefore, the improvement made on the adhesive property is not apparent.

## DESCRIPTION OF THE INVENTION

**[0021]** The present invention is to solve the existing technical problems in UHMWPE fiber production, and specifically to solve the problem in the preparation of homogeneous solution containing raw material, and in the removal of the first solvent from the gel fiber. One objective of the present invention is to provide a simple, efficient and low cost method to prepare the HMWPE fiber. The HMWPE fiber prepared by this method has high adhesive property.

**[0022]** In particular, the technical problems can be solved by the following methods.

**[0023]** The method of preparing UHMWPE fiber comprises: mixing PE powder having a relative average molecule weight (MW) of 1 million to 6 million with polar polymer in a solvent, to form an emulsion mixture; the mixture being fed into an extruder with agitation, where the mixture swells and dissolves rapidly to form a transparent and homogeneous solution; and the solution being extruded through an spinnerette to spin into a gel filament, followed by cooling, extraction, drying and stretching (or drawing) to produce the desired UHMWPE fiber.

**[0024]** During the preparation of the emulsion mixture according to the present invention, the PE powder having a relative MW of 1 million to 6 million is mixed with polar polymer and solvent in an appropriate ratio, and the resulting mixture is fed into an untwisting equipment to untwist, and thereby forming a uniform emulsion mixture.

**[0025]** The concentration of the above-mentioned uniform emulsion mixture is about 4% to 60% (wt).

**[0026]** The polar polymer mentioned above includes polar polymer containing ester group, carbonyl group or ether group. The polar polymer containing ester group, carbonyl group or ether group refers to ethylene/vinyl acetate co-polymer, polyacrylates, polyethylene pyrrolidone /vinyl acetate co-polymer with different K value, polyoxyethylene polymer, or mixtures thereof.

**[0027]** The added weight% for the polar polymer relative to the UHMWPE powder with relative MW of 1 million to 6 million is about 1-10%, preferably about 2-8%.

**[0028]** In the untwisting process mentioned above, silicone oil or its derivative can be used for untwisting. Additionally, silicone oil or its derivative can also be used during the cooling (solidifying) process. Silicone oil or its derivative may comprise about 0.05-5 wt% of the UHMWPE fiber.

**[0029]** During the untwisting process mentioned above, one or more antioxidant, stabilizer, coloring agent, fire retardant can be added.

**[0030]** In the process mentioned above, the untwisting equipment may provide a cutting speed of at least 1000$S^{-1}$, preferably 1000-5000 $S^{-1}$, and more preferably 2000-4000$S^{-1}$. The untwisting equipment mentioned above can be high-speed dispersion machine, agitator (intensive mixing vessel), colloid mill, homogenizer, venturi, or any combinations thereof.

**[0031]** In the method mentioned above, the preferred relative average MW for UHMWPE is 4 million to 6 million, and more preferably 2 million to 5 million.

**[0032]** In the process to prepare the uniform emulsion mixture according to the present invention, the solvent used is liquid under room temperature, and it may be alkane (or paraffin) or its derivative, cycloalkane (or cycloparaffin) or its derivative, aromatic hydrocarbon or its derivative, or mixtures thereof.

**[0033]** In the process to prepare the homogeneous solution according to the present invention, the nominal concentration for the UHMWPE and the solvent is 1-50 wt%.

**[0034]** The extruder used in the present invention includes single screw, double-screw, triple-screw or four-screw extruder, where the extruding temperature is above the melting point of the UHMWPE, for example, 80-250°C as the working temperature for the extruder.

**[0035]** The double-screw extruder can rotate in same direction or reverse direction, and the screw's length/diameter ratio is 1:30-65.

**[0036]** In one embodiment of the present invention, the uniform emulsion mixture stays in the double-screw extruder for 10-60 minutes (residence time), and preferably 20-40 minutes; with a material temperature inside the extruder at 50-280°C, and the extruding temperature for gel spinning at 140-280°C, preferably at 200-260°C.

**[0037]** In another embodiment, the spinnerette of the extruder has a rectangle shape, with a Length/Width ratio of 4-20, preferably 5-15.

**[0038]** In another embodiment, the emulsion mixture can be fed into the extruder directly, or *via* a storage vessel with an agitator (e.g., mixing vessel). The vessel can be one set or more than two sets.

**[0039]** In the drawing (or stretching) process of this invention, the drawing temperature for fiber is 80-130°C, at a draw ratio of more than 20/1, preferably 30/1-60/1.

**[0040]** Compared with existing technologies, the present invention has the following advantages:

1 UHMWPE fiber with PU or butyronitrile glove, is flexible and light, and has anti-corrosive, anti-aging, and anti-oil properties, and is the best option for the preparation of cutting-proof glove on the market. However, due to the inertia ofPE, the adhesive interaction between PE and PU or PE and butyronitrile is poor. The present invention utilizes a cutting untwisting process to prepare UHMWPE. In addition, polar polymer containing ester group, carbonyl group and/or ether group is added to the UHMWPE. As a result, the polar polymer is evenly distributed in the UHMWPE so as to provide a PE fiber with high adhesive property. This process is simple and does not need any additional equipment.

2 The emulsion mixture containing UHMWPE and a suitable amount of polar polymer undergo high speed cutting, swelling as well as complete dissolving in a double screw extruder. This is helpful to minimize the degradation of the polymer, and thereby improving the adhesive property without affecting the mechanical property of the fiber.

3 In addition to the use of high speed cutting to untwist UHMWPE, a suitable amount of carbon chain polar polymer containing polar side groups such as ester group, carbonyl group or carboxy group can be added to improve the adhesive property of the PE without affecting its rupture strength (tenacity).

4 The UHMWPE fiber prepared by the method of the present invention has high rupture strength (tenacity) and strong energy absorption, and provides maximum rupture extension (elongation) while maintaining enough rupture strength, which allows to achieve an optimized balance between rupture strength and rupture extension. This material is suitable for the preparation of cutting-proof glove. This invention uses rapid swelling and dissolving of UHMWPE by a high speed cutting and untwisting process to ensure that the rupture strength for the fiber is above 30CN/dtex with a rupture level of more than 30030CN/dtex.

5 Usually, the fiber used in the cutting-proof glove has a single layer. In addition to good cutting-proof performance, the glove is also required to be even and homogeneous in density. This, it imposes a higher demand on fiber homogeneity. Currently, the CV value for titer and strength of UHMWPE fiber is about 8-10%. The present invention can achieve a CV value for titer and strength of the UHMWPE fiber at about 4-6%, by utilizing rapid swelling and dissolving of UHMWPE and addition of a surface active agent in a cooling (solidifying) solution, as well as the design of a flat filament structure.

6 In accordance with the present invention, the UHMWPE fiber has a flat structure. As a result, the specific surface area of the fiber is increased, which is beneficial for solidifying evenly and shortening the distance for the diffusion of the solvent from the gel fiber. Accordingly, this method can increase the extraction rate, reduce the amount of the second solvent used in extraction and lower the cost, and also improve the homogeneity and strength of the fiber.

7 Utilizing suitable untwisting, the method of the present invention not only makes the process simple, saves cost, manpower and time, but also makes dissolving more homogeneous.

## SPECIFIC EMBODIMENTS

**[0041]** To facilitate the understanding of the technical approach, innovation characteristics, and final results and functions of the present invention, the following examples are provided to further illustrate the invention.

### Example 1

**[0042]** UHMWPE (Relative Average Molecule Weight 4.5M) powder and #90 solvent white oil with a weight ratio of 1:8, were fed into an untwisting pan at room temperature, and underwent cutting for 10minutes at a speed of 2000$S^{-1}$ under $N_2$ protection, to form a homogeneous emulsion mixture. The mixture was fed into a same directional double screw extruder (intake diameter = Φ25mm, Length/Diameter ratio = 36, temperature = 250°C, the screw rotation speed = 35rpm). The extruded material was filtered, and spun into a gel filament through a spinnerette, then extracted and stretched at a stretch ratio of 35, to provide UHMWPE.

### Example 2

**[0043]** UHMWPE (Relative Average Molecule Weight 4.5M) powder and #90 solvent white oil with a weight ration of 1:8 were fed into an untwisting pan at room temperature, and further added EVA28190 (ethylne-vinyl acetate co-polymer, with vinyl acetate comprising 28%, melting index = 190) with an amount of 4 % by weight of the UHMWPE powder, and underwent cutting for 10 minutes under $N_2$ protection at a speed of 2000$S^{-1}$, to form a homogeneous emulsion mixture. The mixture was fed into a same directional double screw extruder (intake diameter = Φ25mm, Length/Diameter ratio = 36, temperature = 250°C, the screw rotation speed = 35rpm). The extruded material was filtered, and spun into a gel filament through a spinnerette, then extracted and stretched at a draw ratio of 35, to produce UHMWPE with high adhesive properties.

### Example 3

**[0044]** UHMWPE (Relative Average Molecule Weight 4.5M) powder and #90 solvent white oil with weight ratio of 1: 8 were fed into an untwisting pan at room temperature, and further added EVA28190 (ethylene-vinyl acetate co-polymer, with vinyl acetate comprising 28%, melting index = 190) with an amount of 2 % by weight of the UHMWPE powder, and underwent cutting for 10 minutes under $N_2$ protection at a speed of 2000$S^{-1}$, to produce a homogeneous emulsion mixture. The mixture was fed into a same directional double screw extruder (intake diameter = Φ25mm, Length/Diameter ratio = 36, temperature = 250°C, the screw rotation speed = 35rpm). The extruded material was filtered, and spun into a gel filament through a spinnerette, then extracted and stretched at a draw ratio of 35, to produce UHMWPE with high adhesive properties.

### Example 4

**[0045]** UHMWPE (Relative Average Molecule Weight 4.5M) powder, is mixed with #90 solvent white oil with weight ratio of 1:8 were fed into an untwisting pan at room temperature, and further added EVA1030 (ethylene-vinyl acetate co-polymer, with vinyl acetate comprising 10%, melting index = 30) with an amount of 4 % by weight of the UHMWPE powder, and underwent cutting for 10 minutes under $N_2$ protection at a speed of $2000S^{-1}$, to produce a homogeneous emulsion mixture. The mixture was fed into a same directional double screw extruder (intake diameter = Φ25mm, Length/Diameter ratio = 36, temperature = 250°C, the screw rotation speed = 35 rpm). The extruded material was filtered, and spun into a gel filament through a spinnerette, then extracted and stretched at a draw ratio of 35, to produce UHMWPE with high adhesive properties.

Example 5

**[0046]** UHMWPE (Relative Average Molecule Weight 4.5M) powder and #90 solvent white oil with weight ratio of 1:8 were fed into an untwisting pan at room temperature, and further added polyacrylate with an amount of 2 % by weight of the UHMWPE powder, and underwent cutting for 10 minutes under $N_2$ protection at a speed of $2000S^{-1}$, to produce a homogeneous emulsion mixture. The mixture was fed into a same directional double screw extruder (intake diameter = Φ25mm, Length/Diameter ratio = 36, temperature = 250°C, the screw rotation speed = 35rpm). The extruded material was filtered, and spun into a gel filament through a spinnerette, then extracted and stretched at a draw ratio of 35, to produce UHMWPE with high adhesive properties.

Example 6

**[0047]** UHMWPE (Relative Average Molecule Weight 4.5M) powder and #90 solvent white oil with weight ratio of 1:8 were fed into an untwisting pan at room temperature, and further added polyoxyethylene with an amount of 4 % by weight of the UHMWPE powder, and underwent cutting for 10 minutes under $N_2$ protection at a speed of $2000S^{-1}$, to form a homogeneous emulsion mixture. The mixture was fed into a same directional double screw extruder (intake diameter = Φ25mm, Length/Diameter ratio = 36, temperature = 250°C, the screw rotation speed = 35rpm). The extruded material was filtered, and spun into a gel filament through a spinnerette, then extracted and stretched at a draw ratio of 35, to produce UHMWPE with high adhesive properties.

**[0048]** The mechanical and adhesive properties of the UHMWPE fiber prepared according to Example 1 (without the addition of polar polymer) and Example 2-6 are listed in Table 1.

Table 1. Mechanical Properties and Adhesive Strength of UHMWPE Fiber Prepared According to This Invention

| Example No. | Rupture Strength (Tenacity) CN/dtex | Young's Modulus CN/dtex | Rupture Extension (Elongation) CN/dtex | Pull-out Strength CN/dtex |
|---|---|---|---|---|
| 1 | 35.25 | 972 | 4.07 | 10.23 |
| 2 | 31.31 | 939 | 4.42 | 26.73 |
| 3 | 33.63 | 953 | 4.26 | 20.54 |
| 4 | 31.09 | 926 | 4.19 | 21.59 |
| 5 | 30.95 | 896 | 4.91 | 29.06 |
| 6 | 33.73 | 977 | 4.15 | 18.77 |

**[0049]** The following procedure is used to measure the adhesive strength of the UHMWPE fiber: The UHMWPE fiber is passed through a capsule with small hole, the height of the capsule being about 7mm. An epoxy resin and a solidifying agent are mixed at a ratio of 4:1, and charged into the capsule, and allow for solidifying for 48 hours. The embedded length L(mm) of the fiber in the capsule is measured, using a pull-out experiment, which utilizes DXLL-20000 Strong Power Device to measure the adhesive properties between the UHMWPE fiber and epoxy resin (clamping distance = 200mm; dropping speed = 50 mm/min.; and the pull-out strength of the fiber can be calculated by the following formula: Pull-out strength = tested strength * 7 /L.

Example 7

**[0050]** UHMWPE (Relative Average Molecule Weight 4.5M) powder and #90 solvent white oil with a nominal concentration of 10% (wt) were fed into an untwisting pan at room temperature, and underwent cutting for 5 minutes under $N_2$ protection at a speed of $3000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a same directional double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 45, temperature = 250°C, the screw rotation speed = 35rpm). The extruded material passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength (i.e., Tenacity) of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

Example 8

**[0051]** UHMWPE (Relative Average Molecule Weight 5 M) powder and #90 solvent white oil with a nominal concentration of 5% (wt) were fed into an untwisting pan at room temperature, and underwent cutting for 5 minutes under $N_2$ protection at a speed of $3000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 64, temperature = 250°C, screw rotation speed = 50 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 28cN/dtex and Young's Modulus of over 900cN/dtex.

Example 9

**[0052]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and #90 solvent white oil with a nominal concentration of 5% (wt) were fed into an untwisting pan at room temperature, and further added 0.2% (wt) of an anti-oxidant, and underwent cutting for 5 minutes under $N_2$ protection at a speed of $2000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 240°C, screw rotation speed = 50 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 28cN/dtex and Young's Modulus of over 900cN/dtex.

Example 10

**[0053]** UHMWPE (Relative Average Molecule Weight 5 M) powder and #90 solvent white oil with a nominal concentration of 12% (wt) were fed into an untwisting pan at room temperature, and underwent cutting for 10 minutes under $N_2$ protection at a speed of $2000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 30 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 35cN/dtex and Young's Modulus of over 1050cN/dtex.

Example 11

**[0054]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and #90 solvent white oil with a nominal concentration of 10% (wt) were fed into an untwisting pan at room temperature *via* a spiral propeller at a speed of 0.5kg/min, and underwent cutting under $N_2$ protection at a speed of $1000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 30 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath containing 2% polyether-epoxy modified silicone oil, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

Example 12

**[0055]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and #70 solvent white oil with a nominal concentration of 12% (wt) were fed into an untwisting pan at room temperature, and underwent cutting for 15 minutes under $N_2$ protection at a speed of $1000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 30 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

Example 13

**[0056]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and #70 solvent white oil with a nominal concentration of 10% (wt) were fed into an untwisting pan at room temperature, and further added 1% (wt) of epoxy modified silicone oil, and underwent cutting for 5 minutes under $N_2$ protection at a speed of $3000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 50 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

Example 14

**[0057]** UHMWPE (Relative Average Molecule Weight 5 M) powder and #90 solvent white oil with a nominal concentration of 12% (wt) were fed into an untwisting pan at room temperature, and underwent cutting for 10 minutes under $N_2$ protection at a speed of $2000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 30 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath containing 1.5wt% of epoxy modified silicone oil, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 35cN/dtex and Young's Modulus of over 1050cN/dtex.

Example 15

**[0058]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and #90 solvent white oil with a nominal concentration of 10% (wt) were fed into an untwisting pan at room temperature *via* a spiral propeller at a speed of 0.5kg/min, and underwent cutting under $N_2$ protection at a speed of $1000S^{-1}$, to form a homogeneous emulsion mixture. The mixture, with agitation, was fed into a double screw extruder *via* a storage vessel (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 30 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette, passed through a water bath containing 2% polyether-epoxy modified silicone oil, followed by extraction, drying and stretching at a draw ratio of 30, to produce UHMWPE fiber with Rupture Strength of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

Example 16

**[0059]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and solvent white oil were mixed to prepare a homogeneous solution with a concentration of 8% (wt) and fed into a double screw extruder (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 240°C, screw rotation speed = 30 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette comprising apertures having a rectangular shape with a Length/Width ratio of 8, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

Example 17

**[0060]** UHMWPE (Relative Average Molecule Weight 4.5 M) powder and solvent white oil were mixed to prepare a homogeneous solution with a concentration of 10% (wt) and fed into a double screw extruder (extruder diameter = Φ25mm, Length/Diameter ratio = 24, temperature = 250°C, screw rotation speed = 40 rpm). The extruded material was passed through a filter tank and a metering pump to get a measurement, and spun into a gel filament through a spinnerette comprising apertures having a rectangular shape with a Length/Width ratio of 12, passed through a water bath, followed by extraction, drying and stretching at a draw ratio of 40, to produce UHMWPE fiber with Rupture Strength of 30cN/dtex and Young's Modulus of over 1000cN/dtex.

**[0061]** The above descriptions demonstrate the basic principles, main characteristics and advantages of the present invention. It should be understood by one of ordinary skill in the art that the present invention is not limited by the examples described hereinabove. The examples and descriptions described herein only illustrate the principles for this invention, and various changes and modifications may be made without departing from the spirit and scope of the present invention. Such changes and modifications are included in the scope of this invention. The claimed scope of the present invention is further illustrated by the appended claims and equivalents thereof.

## Claims

1. A method to prepare UHMWPE fiber, **characterized in that:** UHMWPE powder having a relative average molecular weight of 1 million to 6 million is added with polar polymer and dispersed in a solvent to form an uniform emulsion mixture, using gel spinning, the mixture is fed gradually and with agitation into an extruder wherein the mixture swells and dissolves to form a transparent and homogeneous solution, the solution being extruded through a spinnerette to spin into a gel filament, followed by cooling, solidifying, extraction, drying and stretching to provide the UHMWPE fiber.

2. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** during the preparation of the uniform emulsion mixture, the UHMWPE powder with relative MW 1 million to 6 million, the polar polymer and the solvent are mixed in a suitable ratio and fed into an untwisting equipment to untwist to form the uniform emulsion mixture.

3. The method to prepare UHMWPE fiber according to Claim 1 or Claim 2, **characterized in that:** the concentration of the uniform emulsion mixture is 4%-60%.

4. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the polar polymer is polar polymer comprising an ester group, a carbonyl group or an ether group.

5. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the polar polymer comprising an ester group, a carbonyl group or an ether group is selected from ethylene/vinyl acetate co-polymer, polyacrylates, polyethylene pyrrolidone/vinyl acetate co-polymer, polyoxyethylene polymer and mixtures thereof.

6. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the amount of the polar polymer relative to the UHMWPE powder is 1-10% by weight.

7. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the amount of the polar polymer relative to the UHMWPE powder is 2-8% by weight.

8. The method to prepare UHMWPE fiber according to Claim 2, **characterized in that:** during the untwisting process, silicone oil or its derivative is added for untwisting; and/or during solidifying process, silicone oil or its derivative is added; in which the silicone oil or its derivative comprises 0.05-5% by weight of the UHMWPE fiber.

9. The method to prepare UHMWPE fiber according to Claim 8, **characterized in that:** one or more selected from an antioxidant, a stabilizer, a coloring agent and a fire retardant is added during the untwisting process.

10. The method to prepare UHMWPE fiber according to Claim 2, **characterized in that:** the untwisting equipment provides a cutting speed of at least 1000$S^{-1}$.

11. The method to prepare UHMWPE fiber according to Claim 10, **characterized in that:** the untwisting equipment provides a cutting speed of 1000 to 5000$S^{-1}$.

12. The method to prepare UHMWPE fiber according to Claim 10, **characterized in that:** the untwisting equipment provides a cutting speed of 2000 to 4000$S^{-1}$.

13. The method to prepare UHMWPE fiber according to Claim 2, **characterized in that**: the untwisting equipment is selected from high-speed dispersion machine, mixer, colloid mill, homogenizer, venturi, and combinations thereof.

14. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the UHMWPE has a relative average molecular weight of 4 million to 6 million.

15. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the UHMWPE has a relative average molecular weight of about 2 million to 5 million.

16. The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the solvent used to form an uniform emulsion mixture is in liquid form at room temperature, and is selected from alkane hydrocarbon or its derivative, cycloalkane hydrocarbon or its derivative, aromatic hydrocarbon or its derivative, and mixtures thereof.

**17.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** during the preparation of the uniform emulsion mixture, the nominal concentration of the UHMWPE powder in the solvent is about 1-50wt%.

**18.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the extruder is selected from a single screw extruder, a double-screw extruder, a three-screw extruder, and a four-screw extruder, and the operating temperature for the extruder is 80-250°C.

**19.** The method to prepare UHMWPE fiber according to Claim 18, **characterized in that:** the double-screw extruder can rotate in same direction or reverse direction, and the Length/Diameter ratio of the screw rod is 1:30-65.

**20.** The method to prepare UHMWPE fiber according to Claim 19, **characterized in that:** the residence time for the uniform emulsion mixture in the double-screw extruder is 10-60 minutes, preferably 20-40 minutes; material temperature is 50-280°C, and the temperature of the extruded gel filament is 140-280°C, preferably 200-260°C.

**21.** The method to prepare UHMWPE fiber according to Claim 20, **characterized in that:** the residence time for the uniform emulsion mixture in the double-screw extruder is 20-40 minutes, and the temperature of the extruded gel filament is 200-260°C.

**22.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the spinnerette of the extruder comprises apertures having a rectangle shape with a Length/Width ratio of 4:20.

**23.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the Length/Width ratio is 5:15.

**24.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the emulsion mixture can be fed into the extruder directly or *via* a storage vessel equipped with an agitator.

**25.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the stretching is conducted at a temperature of 80-130°C and at a draw ratio of at least 20/1.

**26.** The method to prepare UHMWPE fiber according to Claim 25, **characterized in that:** the draw ratio is from 30/1 to 60/1 for stretching.

## Amended claims under Art. 19.1 PCT

**1.** A method to prepare UHMWPE fiber, **characterized in that:** UHMWPE powder having a relative average molecular weight of 1 million to 6 million is added with polar polymer and dispersed in a solvent to form an uniform emulsion mixture, using gel spinning, the mixture is fed gradually and with agitation into an extruder wherein the mixture swells and dissolves to form a transparent and homogeneous solution, the solution being extruded through a spinnerette to spin into a gel filament wherein the spinnerette comprises apertures having a shape of rectangle, followed by cooling, solidifying, extraction, drying and stretching to provide the UHMWPE fiber.

**2.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** during the preparation of the uniform emulsion mixture, the UHMWPE powder with relative MW 1 million to 6 million, the polar polymer and the solvent are mixed in a suitable ratio and fed into an untwisting equipment to untwist to form the uniform emulsion mixture.

**3.** The method to prepare UHMWPE fiber according to Claim 1 or Claim 2, **characterized in that:** the concentration of the uniform emulsion mixture is 4%-60%.

**4.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the polar polymer is polar polymer comprising an ester group, a carbonyl group or an ether group.

**5.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the polar polymer comprising an ester group, a carbonyl group or an ether group is selected from ethylene/vinyl acetate co-polymer, polyacrylates, polyethylene pyrrolidone/vinyl acetate co-polymer, polyoxyethylene polymer and mixtures thereof.

**6.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the amount of the polar polymer relative to the UHMWPE powder is 1-10% by weight.

**7.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the amount of the polar polymer relative to the UHMWPE powder is 2-8% by weight.

**8.** The method to prepare UHMWPE fiber according to Claim 2, **characterized in that:** during the untwisting process, silicone oil or its derivative is added for untwisting; and/or during solidifying process, silicone oil or its derivative is added; in which the silicone oil or its derivative comprises 0.05-5% by weight of the UHMWPE fiber.

**9.** The method to prepare UHMWPE fiber according to Claim 8, **characterized in that:** one or more selected from an antioxidant, a stabilizer, a coloring agent and a fire retardant is added during the untwisting process.

**10.** The method to prepare UHMWPE fiber according to Claim 2, **characterized in that:** the untwisting equipment provides a cutting speed of at least 1000S-1.

**11.** The method to prepare UHMWPE fiber according to Claim 10, **characterized in that:** the untwisting equipment provides a cutting speed of 1000 to 5000S-1.

**12.** The method to prepare UHMWPE fiber according to Claim 10, **characterized in that:** the untwisting equipment provides a cutting speed of 2000 to 4000S-1.

**13.** The method to prepare UHMWPE fiber according to Claim 2, **characterized in that:** the untwisting equipment is selected from high-speed dispersion machine, mixer, colloid mill, homogenizer, venturi, and combinations thereof.

**14.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the UHMWPE has a relative average molecular weight of 4 million to 6 million.

**15.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the UHMWPE has a relative average molecular weight of about 2 million to 5 million.

**16.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the solvent used to form an uniform emulsion mixture is in liquid form at room temperature, and is selected from alkane hydrocarbon or its derivative, cycloalkane hydrocarbon or its derivative, aromatic hydrocarbon or its derivative, and mixtures thereof.

**17.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** during the preparation of the uniform emulsion mixture, the nominal concentration of the UHMWPE powder in the solvent is about 1-50wt%.

**18.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the extruder is selected from a single screw extruder, a double-screw extruder, a three-screw extruder, and a four-screw extruder, and the operating temperature for the extruder is 80-250°C.

**19.** The method to prepare UHMWPE fiber according to Claim 18, **characterized in that:** the double-screw extruder can rotate in same direction or reverse direction, and the Length/Diameter ratio of the screw rod is 1:30-65.

**20.** The method to prepare UHMWPE fiber according to Claim 19, **characterized in that:** the residence time for the uniform emulsion mixture in the double-screw extruder is 10-60 minutes, preferably 20-40 minutes; material temperature is 50-280°C, and the temperature of the extruded gel filament is 140-280°C, preferably 200-260°C.

**21.** The method to prepare UHMWPE fiber according to Claim 20, **characterized in that:** the residence time for the uniform emulsion mixture in the double-screw extruder is 20-40 minutes, and the temperature of the extruded gel filament is 200-260°C.

**22.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the spinnerette of the extruder comprises apertures having a rectangle shape with a Length/Width ratio of 4:20.

**23.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the Length/Width ratio is 5:15.

**24.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the emulsion mixture can be fed into the extruder directly or via a storage vessel equipped with an agitator.

**25.** The method to prepare UHMWPE fiber according to Claim 1, **characterized in that:** the stretching is conducted at a temperature of 80-130°C and at a draw ratio of at least 20/1.

**26.** The method to prepare UHMWPE fiber according to Claim 25, **characterized in that:** the draw ratio is from 30/1 to 60/1 for stretching.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2007/002906

A. CLASSIFICATION OF SUBJECT MATTER

D01F6/04（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: D01F6/-,B29C, C08F, C08J, 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)

CNPAT;CNKI;WPI;EPODOC;PAJ; ultra high molecular weight polyethylene, UHMW－PE, gelation, polar polymer, ethylene, vinyl acetate, polyacrylate, polyacrylacid ester, copolymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | CN1160093A（CHINESE TEXTILE SCI INST）24 Sep.1997（24.09.1997）<br>Claims 1-5, page 5 line 23 – page 6 line 10 | 1-9, 13-19, 24-26 |
| Y | JIA Guangxia etc. STUKING ON THE ADHESION OF UHMW-PE FIBER<br>CHINA SYNTHETIC FIBER INDUSTRY, Dec. 1995 No.06 page 24-28, ISSN 1001-0041 | 1-9, 13-19, 24-26 |
| Y | JP63053283B（NTN TOYO BEARING CO LTD）21 Oct. 1988（21.10.1988）<br>Example 1 and 2 | 8 |

☒ 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

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"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<br>06 Jan. 2008 (06.01.2008) | Date of mailing of the international search report<br>**17 Jan. 2008 (17.01.2008)** |
| Name and mailing address of the ISA/CN<br>The State Intellectual Property Office, the P.R.China<br>6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China<br>100088<br>Facsimile No. 86-10-62019451 | Authorized officer<br>ZHU, Zhengqiang<br>Telephone No. (86-10)62085485 |

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## INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2007/002906

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | CN1056544A（UNIV CHINA TEXTILE）27 Nov.1991（27.11.1991）the whole document | 1-26 |
| A | CN1693544A（UNIV DONGHUA）09 Nov.2005（09.11.2005）the whole document | 1-26 |
| A | EP0213208B（NISHIKAWA H etc.）30 Oct.1991（30.10.1991）the whole document | 1-26 |

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## INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2007/002906

| Patent Documents referred in the Report | Publication Date | Patent Family | Publication Date |
|---|---|---|---|
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| JP63053283B | 21.10.1988 | JP61124621A | 12.06.1986 |
| CN1056544A | 27.11.1991 | None | |
| CN1693544A | 09.11.2005 | None | |
| EP0213208B | 30.10.1991 | EP0213208A | 11.03.1987 |
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| | | JP61501028T | 06.11.1986 |
| | | DE3682241G | 05.12.1991 |

Form PCT/ISA/210 (patent family annex) (April 2007)

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