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(54) **POLYOLEFIN YARNS AND METHOD FOR MANUFACTURING**

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(57) **ABSTRACT**

The invention relates to a multifilament yarn having a tenacity of at least 30 cN/dtex, and comprising a plurality of spun ultrahigh molecular weight polyolefin filaments characterized in that the titer of any one of said spun filaments is at least 10 dtex.

POLYOLEFIN YARNS AND METHOD FOR MANUFACTURING

[0001] The invention relates to a multifilament, ultrahigh molecular weight polyethylene (UHMWPE) yarn having a high strength and a method for manufacturing thereof. The invention further relates to various products containing said yarn and in particular to the use of said yarn in applications where cut resistance is desired, e.g. articles of apparel or rugged outerwear such as gloves, aprons, chaps, pants, boots, gators, shirts, jackets, coats, socks, shoes, undergarments, vests, waders, hats, gauntlets, and the like. The invention relates further to the monofilaments comprised in the described multifilament yarns.

[0002] Multifilament UHMWPE yarns are known for example from WO 2005/066401 wherein a high-performance multifilament polyethylene yarn is disclosed, said yarn having very good mechanical and physical properties, e.g. high tenacity, modulus, abrasion and creep resistance. Also the yarns of WO 2005/066401 preserve their good properties even when containing a large number of filaments, making them highly suitable for use in various semi-finished and end-use articles, examples thereof including ropes, cords, fishing nets, sports equipment, medical implants and ballistic-resistant composites.

[0003] Among the above mentioned semi-finished and end-use articles, articles of apparel or rugged outerwear used to protect the wearer against cuts form a special class. For example, the resistance to cut of gloves and other protective apparel, worn by individuals when e.g. handling and processing food, needs for a particular industry to be above a certain level to at least qualify for utilization thereof. A clear example constitutes the meat packing industry where together with an increased level of cut resistance, the protective articles need to provide the wearer with dexterity and tactile sensitivity also.

[0004] In consequence, it was observed that although the known multifilament yarns of WO 2005/066401 show a collection of very good properties, they may have a less optimum performance in some applications, in particular cut resistant applications. There is thus a need for further improving the known yarns to provide optimal cut resistance to products containing thereof. In particular there is a need for cut resistant fabrics which are more versatile, i.e. fabrics that can be used in a broader range of applications where their cut resistance property is primarily needed.

[0005] The invention thus provides a multifilament yarn having a high tenacity, e.g. a tenacity of preferably at least 30 cN/dtex, and comprising a plurality of spun ultrahigh molecular weight polyethylene filaments characterized in that the titer of any one of said spun filaments is at least 10 dtex.

[0006] It was observed that the yarn of the invention, hereinafter the inventive yarn, is highly damage tolerant and chemically resistant and provides products containing thereof with improved cut resistance and/or comfort. In particular it was observed that products comprising a fabric containing the inventive yarn behave very well during handling of oily or wet articles, as they optimally resist against liquid accumulation on the surface of the fabric.

[0007] By filament is herein understood an elongated body, the length dimension of which is much greater than its transverse dimensions, e.g. diameter or the dimensions of width and thickness. Typically the transverse dimensions of a filament are such that the ratio of the highest dimension of said cross-section to the lowest dimensions thereof is at most 5, preferably at most 3. A filament, also called monofilament, is understood to be a monolithic elongated body obtained by a spinning process through a singular spin hole, in contrast to an aggregate of multiple filaments into a monofilament-like product. The term filament includes the embodiment of a fiber also and it may have regular or irregular cross-sections. The filaments typically have continuous lengths, however for certain utilizations they may be processed into so-called staple fibers, i.e. filaments having discontinuous lengths commonly obtained by cutting or stretch-breaking thereof. A yarn for the purpose of the invention is an elongated body containing a plurality of individual filaments.

[0008] Preferably, the filaments of the inventive yarn have a titer of at least 12 dtex, more preferably at least 14 dtex, even more preferably at least 16 dtex, more preferably at least 18 dtex, most preferably at least 22 dtex.

[0009] Preferably, the tenacity of the inventive yarn is at least 35 cN/dtex, more preferably at least 40 cN/dtex, most preferably at least 45 cN/dtex. It was observed that such high tenacity yarns in addition to being highly suitable for use in cut resistant protective apparel, they are also suitable for use in apparel designed to protect against ballistic impacts.

[0010] Preferably the inventive yarns have a titer of at least 50 dtex, more preferably at least 100 dtex, most preferably at least 400 dtex. Preferably, for practical reasons, the inventive yarns have a titer of at most 5000 dtex, more preferably at most 4000 dtex, most preferably at most 3000 dtex. Preferably, the inventive yarn has a number of filaments of at least 5, more preferably at least 24, most preferably at least 80. It was observed that the higher titer yarns of the invention may be manufactured with processes which are conservative of capital and energy requirements.

[0011] In a preferred embodiment, the inventive yarns have a tenacity of at least 30 cN/dtex with filaments having a titer of at least 12 dtex, more preferably at least 15 dtex, most preferably at least 20 dtex. It was observed that such yarns provide products containing thereof with increased resistance against cutting.

[0012] In another aspect, the invention provides a multifilament yarn having a high tenacity, e.g. a tenacity of preferably at least 35 cN/dtex, and comprising a plurality of spun ultrahigh molecular weight polyethylene filaments characterized in that the titer of any one of said spun filaments is at least 10 dtex, more preferably at least 12 dtex, most preferably at least 15 dtex. It was observed that such yarns provide products containing thereof with resistance against ballistic impacts.

[0013] In another embodiment, the inventive yarns contain filaments comprising a hard filler. By hard filler is herein understood a filler having a Moh's hardness of at least 2.5, more preferably at least 4, most preferably at least 6. Good examples of suitable hard fillers include glass fillers, mineral fillers or metal fillers. The fillers may have any shape, e.g. a particulate shape, platelet, needle-like, fibre-like. In a preferred embodiment, the hard filler has a fiber-like shape with an average diameter of at most 20 microns, more preferably at most 15 microns, most preferably at most 10 microns. Preferably the hard fiber-like filler has an average aspect ratio of at least 3, more preferably at least 6, even more preferably at least 10, wherein the aspect ratio is the ratio between the length and the diameter of the hard fiber-like filler. The diameter and the aspect ratio of the hard fiber-like filler may easily be determined by using Scanning Electron Microscopy (SEM) pictures. For the diameter it is possible to make a SEM picture of the filler as such, spread out over a surface and measuring the diameter at 100 randomly selected positions and then calculating the average of the so obtained 100 values. For the aspect ratio it is possible to make a SEM picture of one or more fiber-like fillers and measure the length of hard fibers. Preferably the SEM pictures are made with backscattered electrons. Preferably the hard fiber-like fillers are manufactured with a spinning technique. Advantage of such fillers is that the diameter thereof has a substantially constant value which may provide the inventive yarn with excellent properties for use in cut resistant products.

[0014] The invention also relates to a multifilament yarn having a high tenacity, e.g. a tenacity of preferably at least 12 cN/dtex, more preferably at least 15 cN/dtex, most preferably at least 17 cN/dtex, and comprising a plurality of spun ultrahigh molecular weight polyethylene filaments characterized in that the titer of any one of said spun filaments is at least 10 dtex and wherein said filaments contain a hard filler. The preferred embodiments of the hard filler are disclosed hereinabove. Preferably, the dtex of said filaments is at least 12, more preferably at least 14, even more preferably at least 16, most preferably at least 18.

[0015] The inventive yarn may also contain filaments manufactured from synthetic materials other than UHMWPE; but also filaments manufactured from natural materials and preferably having discontinuous lengths, i.e. natural staple fibers. Examples of natural staple fibers include but not limited to fibers of cellulose, cotton, hemp, wool, silk, jute, sisal, cocos, linen and the like, with cotton being preferred. Examples of natural filaments include metal wire, glass filaments and the like. It was observed that yarns comprising cotton and the filaments of the invention show very good comfort. Examples of filaments of synthetic polymers include but not limited to those manufactured for example from polyamides and polyaramides, e.g. poly(p-phenylene terephthalamide) (known as Kevlar®); poly(tetrafluoroethylene) (PTFE); poly{2,6-diimidazo-[4,5b-4',5'e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (known as M5); poly(p-phenylene-2, 6-benzobisoxazole) (PBO) (known as Zylon®); poly(hexamethyleneadipamide) (known as nylon 6,6), poly (4-aminobutyric acid) (known as nylon 6); polyesters, e.g. poly(ethylene terephthalate), poly(butylene terephthalate), and poly(1,4 cyclohexylidene dimethylene terephthalate); polyvinyl alcohols. Preferred examples of synthetic filaments include polyester and/or polyamide filaments having continuous and/or discontinuous lengths.

[0016] The invention also relates to a fabric comprising the inventive yarns.

[0017] The fabric of the invention, hereinafter the inventive fabric, may be of any construction known in the art, e.g. woven, knitted, plaited, braided or non-woven or combinations thereof. Woven fabrics may include plain weave, rib, matt weave and twill weave fabrics and the like. Knitted fabrics may be weft knitted, e.g. single- or double-jersey fabric or warp knitted. An example of a non-woven fabric is a felt fabric. Further examples of woven, knitted or non-woven fabrics as well as the manufacturing methods thereof are described in "*Handbook of Technical Textiles*", ISBN 978-1-59124-651-0 at chapters 4, 5 and 6, the disclosure thereof being incorporated herein as reference. A description and examples of braided fabrics are described in the same Handbook at Chapter 11, more in particular in paragraph 11.4.1, the disclosure thereof being incorporated herein by reference.

[0018] Preferably the inventive fabric is a knitted fabric, more preferably a woven fabric, even more preferably the woven fabric is constructed with a small weight per unit length and overall cross-sectional diameter. It was observed that such a fabric shows a low weight per unit coverage surface area and increased degree of flexibility and softness while having an improved cut resistance when compared with known fabrics of the same construction.

[0019] The invention relates further to articles and in particular to articles of apparel or rugged outerwear comprising the inventive fabric. Examples of such articles include but are not limited to gloves, aprons, chaps, pants, boots, gators, shirts, jackets, coats, socks, shoes, undergarments, vests, waders, hats, gauntlets, and the like.

[0020] The invention also relates to the use of the inventive fabric in articles of apparel or rugged outerwear and in particular in the examples mentioned hereinabove.

[0021] In particular, the invention relates to gloves comprising the fabric of the invention. It was observed that the gloves of the invention may show good comfort and also breathability. Preferably, the fabric contained by the inventive gloves is a knitted fabric to enhance the fit and the flexibility of the glove.

[0022] It was observed that the inventive yarns have properties which also make them an interesting material for use in ropes, cordages and the like, preferably ropes designed for heavy-duty operations as for example marine, industrial and offshore operations. Heavy duty operations may include, but not restricted to, anchor handling, mooring of support platforms for offshore renewable energy generation, mooring of offshore oil drilling rigs and production platforms and the like.

[0023] The inventive yarns are also very suitable for use as a reinforcing element for reinforced products such as hoses, pipes, electrical and optical cables, and in particular for reinforcing products used in deep-water environments. The invention therefore also relates to a reinforced product containing reinforcing elements wherein the reinforcing elements contain the inventive yarns.

[0024] The invention also relates to medical devices comprising the inventive yarns. In a preferred embodiment, the medical device is a cable or a suture, preferably used in implants. Other examples include mesh, endless loop products, bag-like or balloon-like products, but also other woven and/or knitted products. Good examples of cables include a trauma fixation cable, a sternum closure cable, and a prophylactic or per prosthetic cable, long bone fracture fixation cable, small bone fracture fixation cable. Also tube-like products for e.g. ligament replacement are suitably manufactured from the inventive yarns. Such products made from the inventive yarns show an efficient ratio between their load carrying surface and their surface exposed to the human or animal body. It was further observed that the inventive yarns may be less prone to infestation and may also allow for easier flush with sterilizing agents.

[0025] The invention further relates to composite articles containing the inventive yarns. Preferably, a composite article according to the invention comprises a plurality of layers, wherein each of said layers contains the inventive yarns, wherein said yarns are preferably arranged in a parallel array, also known as unidirectional (UD) layers.

[0026] Multilayered composite articles proved very useful in ballistic applications, e.g. body armor, helmets, hard and flexible shield panels, panels for vehicle armouring and the like. Therefore, the invention also relates to ballistic-resistant articles as the ones enumerated hereinabove containing the inventive yarns.

[0027] It was also observed that the inventive yarns are also suitable for use in other applications like for example, fishing lines and fishing nets, ground nets, cargo nets and curtains, kite lines, dental floss, tennis racquet strings, canvas (e.g. tent canvas), nonwoven cloths and other types of fabrics, webbings, battery separators, capacitors, pressure vessels, hoses, (offshore) umbilical cables, electrical, optical fiber, and signal cables, automotive equipment, power transmission belts, building construction materials, cut and stab resistant and incision resistant articles, protective gloves, composite sports equipment such as skis, helmets, kayaks, canoes, bicycles and boat hulls and spars, speaker cones, high performance electrical insulation, radomes, sails, geotextiles and the like. Therefore, the invention also relates to the applications enumerated above containing the yarns of the invention.

[0028] The invention also relates to sports equipment comprising the inventive yarn, including a fishing line, a kite line and a yacht line. The invention also relates to a freight container having walls comprising the inventive yarn.

[0029] In another aspect of the invention, the multifilament yarn comprises gel-spun UHMWPE monofilament having a high tenacity, e.g. a tenacity of preferably at least 30 cN/dtex, more preferably at least 35 cN/dtex, and a titer of at least 10 dtex, more preferably at least 12 dtex, most preferably at least 15 dtex. It was observed that a cutting device using the monofilament of the invention as the cutting element, show good advantages in particular in the food industry, e.g. for cutting boiled eggs or cheese products. In particular it was observed that the cleanability of the cutting device is optimum.

[0030] Therefore, the invention also relates to a gel-spun UHMWPE monofilament and a cutting device comprising a cutting element, i.e. the element that is used to part into smaller sections the product to be cut, said cutting element comprising any one of the inventive yarns, preferably said cutting element comprising the inventive gel-spun monofilament.

[0031] In one embodiment of the invention, the gel-spun UHMWPE monofilament has a strength per filament of at least 4.0 N, preferably of at least 4.5 N, more preferably of at least 5.0 N, even more preferably of at least 6.0 N and most preferably of at least 7 N. It was observed that yarns comprising the monofilaments of the invention as a strength element show advantages in particular in sewing fabric, e.g. multicolor fabrics or as a fishing line. In particular it was observed that the monofilament according to the invention provide seams that are hardly visible to the human eye by their virtue of fineness and transparency. Preferably the monofilament according to this embodiment of the invention has a tenacity of at least 20 cN/dtex, more preferably 25 cN/dtex and most preferably 30 cN/dtex. It was observed that monofilaments with higher tenacity provide seams with further reduced visibility to the human eye. Therefore the invention also relates to a yarn comprising at least one monofilament according to the invention, preferably the yarn substantially consists of the monofilament according to the invention.

[0032] The invention further relates to a method for manufacturing a yarn containing a plurality of UHMWPE spun filaments, comprising in the following order the steps of:

[0033] a. Providing a solution of UHMWPE in a suitable solvent, preferably decaline;

[0034] b. Forcing said solution through a die containing a plurality of apertures wherein the apertures issue said solution at a first speed to form a plurality of filaments containing said solution; each aperture having an exit with an exit diameter D_{ap}^{exit}; each of said filaments having a diameter D_{fil} as measured at the exit of said capillary;

[0035] c. Immersing said solution-containing filaments into a cooling bath; preferably cooling water bath; and taking-up said immersed filaments onto a take-up roll rotating at a second speed; and

[0036] d. Taking-out said filaments from the bath to form spun filaments, at least partially extracting the solvent and drawing said spun filaments in at least one drawing step before; during and/or after said extraction;

wherein step b) is operated at a draw-down (DD_{op}), defined as the ratio between the second speed and the first speed, of between 20% and 90% of a resonance draw-down DD_{res}; wherein DD_{res} is the ratio between the second speed and the first speed whereat D_{fil} fluctuates per minute with a percentage of at least 25% between a maximum value D_{fil}^{max} and a minimum value D_{fil}^{min}; wherein the percentage is calculated with Formula 1

$$100 \times \frac{D_{fil}^{max} - D_{fil}^{min}}{D_{fil}^{avg}} \qquad \text{Formula 1}$$

wherein D_{fil}^{avg} is the average value of D_{fil} calculated from a number of at least 10 measurements recorded during a minute.

[0037] It was observed that the inventive method is very stable, with a reduced amount of filament breakages and/or allowing for similar drawing patterns for all filaments of the yarn. Also the inventive method allows for the production of yarns having an optimal combination of strength and filament titer.

[0038] According to the inventive method, in step b) each aperture issues the solution at a first speed, which is calculated as the ratio between the volumetric flow of solution per aperture and the area

$$\frac{\pi}{4}(D_{ap}^{exit})^2$$

of the aperture. The volumetric flow of solution per aperture can be readily determined by dividing the volumetric flow of solution before entering the die by the number of the apertures. The volumetric flow of solution before entering the die can be readily set by using a spinning pump or an extruder. Preferably, all apertures are essentially identical, in case apertures with different diameters are used, the values above are herein understood as average values.

[0039] At step c), the immersed filaments are taken-up onto a roll rotating at a second speed. By speed is herein understood the surface speed of said roll. Said speed can be easily adjusted by using a driving motor to drive said roll.

[0040] According to the inventive method, the DD_{res} is determined from analyzing the fluctuations per minute of D_{fil}. D_{fil} can be readily determined from calibrated photographs or by using a calibrated video camera. D_{fil} is expressed in mm. In the present invention,

$$100 \times \frac{D_{fil}^{max} - D_{fil}^{min}}{D_{fil}^{avg}}$$

is at least 25%, more preferably at least 30%, even more preferably at least 40%, most preferably at least 50%. It was observed that by choosing a higher threshold for determining the DD_{res}, the advantages of the inventive method were more conspicuous. In particular for DD_{op} between 40% and 90% Of DD_{res}, more preferably between 50% and 90% of DD_{res}, most preferably between 60% and 90% of DD_{res}, the inventive method operated at its optimum.

[0041] The draw-down (DD_{op}) at which step b) of the inventive method operates can be easily set, for example by first increasing the draw-down to reach a draw-down resonance, as defined hereinabove, and then decreasing the draw-down to the required value, e.g. at most 90% of DD_{res}. Preferably, DD_{op} is at most 85% of DD_{res}, more preferably at most 80%, most preferably at most 75%. It was observed that the stability of the inventive method increases while reducing the draw-down. DD_{op} is also at least 20% of DD_{res}, preferably at least 40%, most preferably at least 60%. Such values for DD_{op} are novel and defy the common understanding in the art, since the current spinning processes for manufacturing UHMWPO filaments use values for DD_{op} in the range of at most 5% of DD_{res}. The common belief leading to using values for DD_{op} so far away from DD_{res} are that the process is more stable and by increasing the DD_{op} would only introduce instabilities and filament breakages. However, the present inventors demonstrated to the contrary and achieved a high stability of the inventive method.

[0042] Preferably, the D_{ap}^{exit} of each one of the apertures is at least 1.5 mm, more preferably at least 2 mm, most preferably at least 3 mm. Preferably, said D_{ap}^{exit} is at most 5 mm, more preferably at most 4 mm, most preferably at most 3.5 mm. It was observed that even for such large diameter apertures, the inventive method is very stable even when using an DD_{op} closer to DD_{res}. Preferably, each aperture contains a capillary having a substantially constant diameter of at least 1.5 mm, more preferably at least 2 mm, most preferably at least 3 mm, wherein said diameter of the capillary is equal with D_{ap}^{exit}. Preferably, said diameter is at most 5 mm, more preferably at most 4 mm, most preferably at most 3.5 mm. It was observed that the inventive method provides very good results for capillaries having a diameter of between 2 mm and 4 mm, most preferably between 2.5 mm and 3.5 mm, most preferably of about 3 mm. Preferably said capillary has an L/D_{ap}^{exit} ratio of at least 1.5, more preferably at least 2.0, most preferably of at least 2.5; with L being the length of the capillary. Preferably said L/D_{ap}^{exit} ratio is at most 10, more preferably at most 7.5, most preferably at most 5.

[0043] The apertures may also contain a so-called contraction zone, i.e. a zone with a gradual decrease in diameter from a diameter D_0 to D_{ap}^{exit}. The contraction zone preferably has an angle in the range 8-75°. It is preferred that the apertures also contain the capillaries as defined immediately hereinabove, in this case, the contraction zone being preferably positioned upstream of the capillary.

[0044] At step b) of the inventive method the UHMWPE solution is forced through the apertures of a die at a first flow rate of preferably at least 1.4 g/min/aperture; more preferably at least 2.0 g/min/aperture; even more preferably at least 2.4 g/min/aperture. Preferably said first flow rate is between 2.0 g/min/aperture and 8.0 g/min/aperture; more preferably between 2.4 g/min/aperture and 7.7 g/min/aperture.

[0045] The herein described inventive process may allow the production of both, the inventive multifilament yarn as well as the inventive monofilaments. Here for the extruded filaments may be processed as described herein as a bundle of yarns or may be split at any stage of the process into one or more monofilaments and an optional remainder of the multifilament yarn composed of he remainder of monofilaments.

[0046] Preferably, the solution-containing filaments, hereinafter also referred to as fluid filaments, are issued at step b) of the inventive process into an air-gap. Preferably, said fluid filaments are drawn in the air gap with a draw ratio of preferably at least 8, more preferably at least 12, even more preferably at least 14, yet even more preferably at least 16, most preferably at least 18. Preferably, the air gap has a length of between 1 mm and 20 mm, more preferably between 2 mm and 15 mm, even more preferably between 2 mm and 10 mm, most preferably between 2 mm and 5 mm. It was observed that such preferred air gap length may allow to reduce the draw rate in the air gap without substantially affecting yarn tenacity.

[0047] In an alternative embodiment the fluid filaments are drawn in the air gap with a draw ration of between 3 and 12, preferably between 4 and 10 and most preferably between 4 and 8. Such preferred draw ratio of the filament in the air gap is especially suited for the production of yarns and monofilaments with a high strength per filament measured on the yarn or a single filament as described in the experiments.

[0048] Although called air gap, said gap can be filled with any gas or gaseous mixture, e.g. air, nitrogen or other inert gases. By air gap is herein understood the distance between the die and the cooling bath. The cooling bath can be a liquid, e.g. water, containing bath at a temperature below the spinning temperature, e.g. about room temperature. In case the cooling bath is a liquid cooling bath, the minimum value of the air gap is preferably chosen to prevent any liquid surface waves from touching the surface of the die.

[0049] Any of the known solvents suitable for spinning of UHMWPE can be used as solvent for making said solution, for example paraffin wax, paraffin oil or mineral oil, kerosenes, decalin, tetralin, or a mixture thereof. It is found that the present process is especially advantageous for relatively volatile solvents, preferably solvents having a boiling point at atmospheric conditions of less than 275° C., more preferably less than 250 or 225° C. Suitable examples include decalin, tetralin, and several kerosene grades. The solution can be made using known methods; preferably, a twin-screw extruder is applied to make a homogeneous solution from a slurry of UHMWPE in said solvent. The solution is preferably fed to the die, also called spinplate, at constant flow rate with metering pumps. The concentration of the solution is preferably between 3 and 25 mass %, with a lower concentration being preferred the higher the molar mass of the polyolefin or polyethylene is. Preferably, the concentration is between 3 and 15 mass % for an UHMWPE with an intrinsic viscosity (IV) in the range 15-25 dl/g. The UHMWPE solution is preferably formed at a temperature within at most 90° C. of the boiling point of the solvent, more preferably at most 70° C.

[0050] The UHMWPE preferably has an intrinsic viscosity (IV, as measured on solution in decalin at 135° C.) of between about 8 dl/g and 40 dl/g, preferably between 10 dl/g and 30 dl/g, more preferably between 12 dl/g and 28 dl/g, most preferably between 15 dl/g and 25 dl/g. Intrinsic viscosity is a measure for molar mass (also called molecular weight) that can more easily be determined than actual molar mass parameters like M_n and M_w. There are several empirical relations between IV and M_w, but such relation is dependent on molar mass distribution. Based on the equation $M_w=5.37*10^4$ $[IV]^{1.37}$ (see EP 0504954 A1) an IV of 4 or 8 dl/g would be equivalent to M_w of about 360 or 930 kg/mol, respectively.

[0051] Preferably, the UHMWPE is a linear polyethylene with less than one branch per 100 carbon atoms, and preferably less than one branch per 300 carbon atoms; a branch or side chain or chain branch usually containing at least 10 carbon atoms. The linear polyethylene may further contain up to 5 mol % of one or more comonomers, such as alkenes like propylene, butene, pentene, 4-methylpentene or octene.

[0052] The UHMWPE that is used in the inventive process may further contain small amounts, generally less than 5 mass %, preferably less than 3 mass % of customary additives, such as anti-oxidants, thermal stabilizers, colorants, flow promoters, etc. The UHMWPE can be a single polymer grade, but also a mixture of two or more different polymer grades, e.g. differing in IV or molar mass distribution, and/or type and number of comonomers or side groups.

[0053] In accordance with the invention, after taking out the filaments from the bath to obtain spun filament, said spun filaments is subjected to an extraction step wherein the solvent present therein is at least partly removed from the filaments. solvent removal can be performed by known methods, for example by evaporation if a relatively volatile solvent, e.g. decaline, is used; by using an extraction liquid; or by a combination of both methods.

[0054] The inventive method further comprises at least one drawing step wherein the spun filaments are drawn in at least one stage preferably with a draw ratio of at least 4. Preferably, drawing is performed in at least two stages, and preferably at different temperatures with an increasing profile. The drawing preferably takes place between about 120 and about 155° C. A 3-stage drawing is most preferred, with a total draw ratio $DR_{total}=DR_{stage\ 1}*DR_{stage\ 2}*DR_{stage\ 3}$ of at least 10, more preferably at least 20, most preferably at least 40.

[0055] In a preferred embodiment, the inventive method produces the inventive yarn, wherein a die having apertures with a D_{ap}^{exit} of at least 2 mm, is used; a solution of at least 5 wt % UHMWPE of the total weight of the solution is used; a DD_{op} of at least 20% of DD_{res}, is used; and a 3-stage drawing with a total draw ratio of at least 20 is used. Preferably, D_{ap}^{exit} is at least 3 mm, more preferably between 2.5 mm and 3.5 mm. Preferably, the UHMWPE solution has at least 6 wt %, more preferably at least 8 wt %, most preferably at least 9 wt %. Preferably the solvent is decaline. Preferably, DD_{op} is at least 40% of DD_{res}, most preferably at least 60%.

[0056] The invention will be further explained by the following examples and comparative experiment, however first the methods used in determining the various parameters used hereinabove are presented.

[0057] dtex: yarn's or filament's titer was measured by weighing 100 meters of yarn or filament, respectively. The dtex of the yarn or filament was calculated by dividing the weight (expressed in milligrams) to 10;

[0058] IV: the Intrinsic Viscosity is determined according to method ASTM D1601(2004) at 135° C. in decalin, the dissolution time being 16 hours, with BHT (Butylated Hydroxy Toluene) as anti-oxidant in an amount of 2 g/l solution, by extrapolating the viscosity as measured at different concentrations to zero concentration.

[0059] Tensile properties of fibers: tensile strength (or strength) and tensile modulus (or modulus) are defined and determined on multifilament yarns as specified in ASTM D885M, using a nominal gauge length of the fibre of 500 mm, a crosshead speed of 50%/min and Instron 2714 clamps, of type "Fibre Grip D5618C". On the basis of the measured stress-strain curve the modulus is determined as the gradient between 0.3 and 1% strain. For calculation of the modulus and strength, the tensile forces measured are divided by the titre, as determined by weighing 10 metres of fibre; values in GPa are calculated assuming a density of 0.97 g/cm^3. Strength per monofilament is determined by multiplying the tenacity of the multifilament yarn in cN/dtex by the dtex per filament of the yarn.

EXAMPLES 1-4

[0060] A slurry was prepared from 9 wt % UHMWPE having an IV of about 20 dl/g in decalin and fed to a co-rotating twin screw extruder to transform the slurry into a solution. The extruder and spinning head was heated at a temperature of 185° C. The solution was forced through a die having 24 apertures with a rate of about 7.7 g/min (for examples 1 and 2) and 3.8 g/min (for examples 3 and 4) per aperture.

[0061] The apertures contained a conical contraction zone with an angle of 15° upstream to a capillary having a D_{ap}^{exit} of 3 mm and a length of about 8 mm.

[0062] The fluid filaments issued from the apertures entered an air gap and were taken-up at such rate that a draw ratio as shown in Table 1 below was applied in the air gap. The DD_{op} at which the process is operated is the same as the drawing ratio in the air gap and is in all cases about 90% of the resonance draw down DD_{res}.

[0063] Subsequently the fluid filaments entered a water bath where they were cooled and were taken up onto a take-up roll. Subsequently, they entered a first oven where they were drawn 8 times while the decalin evaporated.

[0064] From the first oven, the filaments entered a second oven where they were drawn with various draw ratios as shown in Table 1 below together with yarn's properties.

TABLE 1

	EX 1	EX 2	EX 3	EX 4
Draw ratio air gap	16	16	14	14
Length air gap (mm)	15	15	7	7
Draw ratio	2.2	3.0	2.0	2.5
dtex yarn (dtex)	424	315	556	439
Tenacity yarn (cN/dtex)	29.4	29.8	25.2	28.3
Modulus yarn (cN/dtex)	1031	1241	897	1066
EAB yarn (%)	3.4	2.8	3.3	3.2
Filament titer (dtex)	18	13	23	18
Strength per filament (N)	5.3	3.9	5.8	5.1

EXAMPLES 5 and 6

[0065] Example 1 was repeated with the difference that the yarn was further drawn in a third step at about 149° C. Two draw ratios are applied as shown in Table 2 below.

TABLE 2

	EXAMPLE 5	EXAMPLE 6
Third step's draw ratio	1.8	2.2
dtex yarn (dtex)	290	213
Tenacity yarn (cN/dtex)	34.3	42.6
Modulus yarn (cN/dtex)	1390	1784
EAB yarn (%)	3.0	2.9
Filament titer (dtex)	12.1	8.9
Strength per filament (N)	4.1	3.8

EXAMPLE 7

[0066] The material of Example 1 was knit into a fabric with an aerial density of 260 g/m^2 (stitch density 10 gauge). For reference, a fabric was knit of the same construction, using a commercially available yarn of 440 dTex containing 195 UHMWPE filaments, the yarn having a tenacity of about 31 cN/dtex and being sold by DSM Dyneema®, NL under the product name SK62.

[0067] Both fabrics were subjected to cut resistance testing according to standard EN388, as well as standard ASTM 1790-05 (both in duplicate). Similarly, fabrics were subjected to the Martindale (EN388) abrasion test, in which for each fabric type the numbers of cycles were determined where breakthrough observed. Results obtained are listed in the Table 3 below:

TABLE 3

Test	Reference	Example 7
EN 388 - Cut index	2.5	6.0
EN 388 - Cut index	3.7	6.1
ASTM F1790-05 Reference force	2.8 N	5.6 N
ASTM F1790-05 Reference force	2.7 N	5.6 N
EN 388 Abrasion breakthrough cycles	1140 cycles	3437 cycles

EXAMPLE 8

[0068] Example 1 was repeated; however, about 7% by weight of the total solution of a hard filler was added to the slurry prior to extrusion. The hard filler was mineral fibrils, i.e. a filler having fiber-like shape, sold under the trade name CF10ELS by Lapinus, NL. The resulting yarn had a titer of 410 dTex, a tenacity of about 18 cN/Dtex and a modulus of about 850 cN/dTex.

[0069] The yarn was knit into a fabric with aerial density of 260 g/m^2 (Stitch density 10 gauge). For reference, a fabric was knit of the same construction, using a commercially available yarn of 440 dTex containing 130 UHMWPE filaments, the yarn having a tenacity of about 17 cN/dtex and containing the same type and amount of hard filler as the above.

[0070] Both fabrics were subjected to same cut resistance testing as detailed at example 7 above. The Martindale abrasion test was carried out 4 time for each fabric. Results obtained are listed in the Table 4 below:

TABLE 4

Test	Reference	Example 8
EN 388 - Cut index	15.69	28.15
EN 388 - Cut index	—	24.82
ASTM F1790-05 Reference force	11.1 N	21.2 N
ASTM F1790-05 Reference force	11.1 N	20.9 N
EN 388 Abrasion breakthrough	400 cycles	1400 cycles
EN 388 Abrasion breakthrough	459 cycles	1600 cycles
EN 388 Abrasion breakthrough	691 cycles	1800 cycles
EN 388 Abrasion breakthrough	1204 cycles	2200 cycles

EXAMPLES 9 and 10

[0071] Example 1 was repeated, however, the fluid filaments were drawn about 19 times in the air gap with a throughput per aperture of 5.7 g/min. In the first oven they were stretched 6 times. The yarn was drawn in a second step with various draw ratios as shown in Table 4 below, together with yarn's properties.

TABLE 5

	EXAMPLE 9	EXAMPLE 10
Draw ratio	3.0	4.0
Dtex yarn (dtex)	347	263
Tenacity yarn (cN/dtex)	30.9	34.7
Modulus yarn (cN/dtex)	1076	1269
EAB yarn (%)	3.5	3.4
Filament titer (dtex)	14	11
Strength per filament (N)	4.3	3.8

EXAMPLES 11 and 14

[0072] Example 1 was repeated, however, the spinning head temperature was reduced to 175° C., the fluid filaments were drawn about 5.7 times in the air gap of a length of 4 mm and with a throughput per aperture of 7.7 g/min. The filaments were drawn in the first and a second step with various draw ratios as shown in Table 6 below, together with yarn's properties. From the 24 filaments exiting the spin plate a single filament was individually processed resulting in examples 11 to 13 while the remaining 23 filaments were processed as a 23 filament yarn. Only the corresponding 23 filament yarn of example 13 is reported as example 14 whereas the corresponding 23 filament yarns of examples 11 and 12 are not reported.

TABLE 6

	EX 11	EX 12	EX 13	EX 14
Filaments per yarn	1	1	1	23
Draw ratio first oven	12	12	14	14
Draw ratio second oven	2.1	2.5	2.1	2.1
dtex yarn (dtex)	35	30	30	672
Tenacity yarn (cN/dtex)	32.6	34.2	29.2	27.5
Modulus yarn (cN/dtex)	1099	1189	1009	1042
EAB yarn (%)	3.5	3.5	3.3	3
Filament titer (dtex)	35	30	30	29
Strength per filament (N)	11.4	10.2	8.8	8.0

1. A multifilament yarn having a tenacity of at least 30 cN/dtex, and comprising a plurality of spun ultrahigh molecular weight polyethylene filaments characterized in that the titer of any one of said spun filaments is at least 10 dtex.

2. The yarn of claim **1** having a tenacity of at least 35 cN/dtex, preferably at least 40 cN/dtex, more preferably at least 45 cN/dtex.

3. The yarn of claim **1** having a filament titer of at least 12, preferably at least 14, more preferably at least 16 dtex.

4. The yarn of claim **1** having a titer of at least 50 dtex, preferably at least 100 dtex, most preferably at least 400 dtex.

5. The yarn of claim **1** wherein the filaments comprise a hard filler having a Moh's hardness of at least 2.5.

6. The yarn of claim **1** further containing filaments manufactured from natural materials and preferably having discontinuous lengths said natural material being chosen from the group of materials consisting of cellulose, cotton, hemp, wool, silk, jute, sisal, cocoas and linen; with cotton being the preferred natural material. A fabric comprising the yarns of claim **1** and a glove comprising the fabric.

7. A product chosen from the group of products consisting of fishing lines and fishing nets, ground nets, cargo nets and curtains, kite lines, dental floss, tennis racquet strings, canvas, nonwoven cloths and other types of fabrics, webbings, battery separators, capacitors, pressure vessels, hoses, (offshore) umbilical cables, electrical, optical fiber, and signal cables, automotive equipment, power transmission belts, building construction materials, cut and stab resistant and incision resistant articles, protective gloves, composite sports equipment such as skis, helmets, kayaks, canoes, bicycles and boat hulls and spars, speaker cones, high performance electrical insulation, radomes, sails and geotextiles, said product comprising the yarns of claim **1**.

8. The spun UHMWPE monofilament of the multifilament yarn of claim **1**, wherein the monofilament is a gel-spun monofilament with a tenacity of at least 30 cN/dtex and a titer of at least 10 dtex.

9. The monofilament of claim **7** wherein the monofilament has a strength of at least 4.0 N, preferably at least 4.5 N, more preferably of at least 5.0 N.

10. A method for manufacturing claim **1**, comprising in the following order the steps of:

a. Providing a solution of ultrahigh molecular weight polyethylene, in a suitable solvent, preferably decaline;

b. Forcing said solution through a die containing a plurality of apertures wherein the apertures issue said solution at a first speed to form a plurality of filaments containing said solution; each aperture having an exit with an exit diameter D_{ap}^{exit}; each of said filaments having a diameter D_{fil} as measured at the exit of said capillary;

c. Immersing said solution-containing-filaments into a cooling bath;

preferably cooling water bath; and taking-up said immersed filaments onto a take-up roll rotating at a second speed; and

d. Taking-out said filaments from the bath to form spun filaments, at least partially extracting the solvent and drawing said spun filaments in at least one drawing step before; during and/or after said extraction;

wherein step b) is operated at a draw-down (DD_{op}), defined as the ratio between the second speed and the first speed, of between 20% and 90% of a resonance draw-down DD_{res}; wherein DD_{res} is the ratio between the second speed and the first speed whereat D_{fil} fluctuates per minute with a percentage of at least 25%, between a maximum value D_{fil}^{max} and a minimum value D_{fil}^{min};

wherein said percentage is calculated with Formula 1

$$100 \times \frac{D_{fil}^{max} - D_{fil}^{min}}{D_{fil}^{avg}} \quad \text{Formula 1}$$

wherein D_{fil}^{avg} is the average value of D_{fil} calculated from a number of at least 10 measurements recorded during a minute.

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