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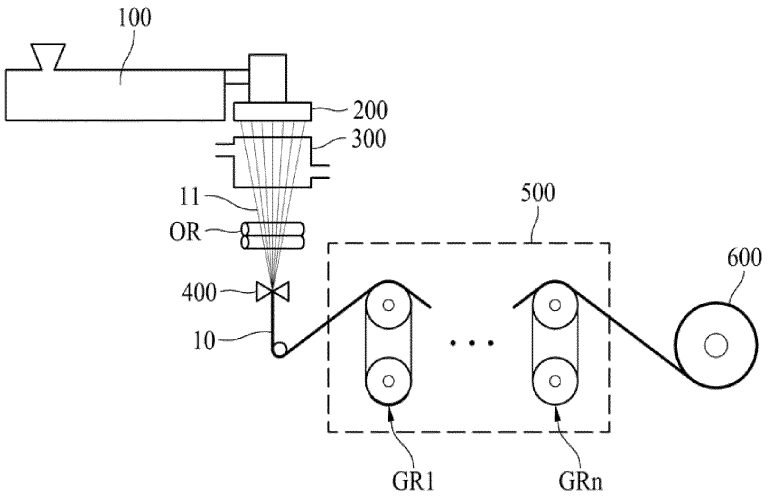
(54) POLYETHYLENE YARN HAVING EXCELLENT THERMAL PROPERTIES AND METHOD FOR MANUFACTURING SAME

(57) The present disclosure relates to a polyethylene yarn and a method for manufacturing the same. According to the present disclosure, a polyethylene yarn having excellent thermal properties, and a method capable of efficiently manufacturing the polyethylene yarn are provided.

【FIG. 1】



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Description

[TECHNICAL FIELD]

[0001] The present disclosure relates to a polyethylene yarn and a method for manufacturing the same.

[BACKGROUND OF ART]

[0002] High-strength polyethylene yarns can be classified into ultra-high molecular weight polyethylene (hereinafter, 'UHMWPE') yarns and high molecular weight polyethylene (hereinafter, 'HMWPE') yarns.

[0003] The UHMWPE generally refers to linear polyethylene having a weight average molecular weight(Mw) of more than 600,000 g/mol. The HMWPE generally refers to linear polyethylene having a weight average molecular weight(Mw) of 20,000 to 600,000 g/mol.

[0004] Due to its high melt viscosity, it is known that the UHMWPE yarn can be manufactured only by a gel spinning method.

[0005] For example, ethylene may be polymerized in an organic solvent in the presence of a catalyst to prepare a UHMWPE solution, the solution may be spun and cooled to form a fibrous gel, and the fibrous gel may be drawn to obtain a high-strength and high-modulus polyethylene yarn. However, this gel spinning method requires the use of an organic solvent, which not only causes environmental problems, but also requires huge expenses for recovering the organic solvent.

[0006] The HMWPE has a relatively low melt viscosity compared to the UHMWPE, which makes it possible to manufacture a yarn through melt spinning. However, the HMWPE has a limit in that the strength of the yarn must inevitably be reduced due to its relatively low molecular weight.

[0007] In addition, polyethylene yarn has lower thermal properties (e.g., melting point) than yarns made from materials such as polyethylene terephthalate and polyamide. Accordingly, there is a problem that the physical properties of polyethylene yarn are deteriorated in the post-processing process (e.g., dyeing, coating, curing, etc.) required for applying polyethylene yarn for various purposes.

[DETAILED DESCRIPTION OF THE INVENTION]

[Technical Problem]

[0008] It is an object of the present disclosure to provide a polyethylene yarn having excellent thermal properties.

[0009] It is another object of the present disclosure to provide a method capable of efficiently manufacturing the polyethylene yarn.

[Technical Solution]

[0010] According to an embodiment of the present disclosure, there is provided a polyethylene yarn satisfying the following Equation 1:

[Equation 1]

$$0.05 \leq [(A-B)/A] \leq 0.35$$

in Equation 1,

A is the melting heat value(ΔH_f, J/g) at a first temperature rise (1st run: heating from 50 °C to 180 °C at 10 °C/min) according to a differential scanning calorimetry on the polyethylene yarn, and

B is the melting heat value(ΔH_f, J/g) at a second temperature rise (2nd run: heating from 50 °C to 180 °C at 10 °C/min on the polyethylene yarn cooled to 50 °C after the first temperature rise) according to a differential scanning calorimetry on the polyethylene yarn.

[0011] According to another embodiment of the present disclosure, there is provided a method for manufacturing the polyethylene yarn, the method comprising the steps of:

providing a melt containing polyethylene having a weight average molecular weight(Mw) of 50,000 g/mol to 600,000 g/mol and a melt index (190 °C, load: 2.16 kgf) of 0.3 g/10 min to 5.0 g/10 min,

extruding the melt through a spinneret to obtain filaments,
cooling the filaments,
drawing a multi-filament composed of the cooled filaments, and
winding the drawn multi-filaments.
wherein the cooling is performed in a quenching zone having a plurality of cooling sections divided by the temperature of the sections, and the plurality of cooling sections are set to have a temperature gradient that gradually decreases toward a discharge part from an introduction part of the filaments.

[0012] Now, a polyethylene yarn and a method for manufacturing the same according to embodiments of the present disclosure will be described in more detail.

[0013] Unless explicitly stated herein, the technical terms used herein are for the purpose of describing specific embodiments only and is not intended to limit the scope of the invention.

[0014] As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0015] It should be understood that the terms "comprise," "include", "have", etc. are used herein to specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or groups thereof.

[0016] As a result of research conducted by the present inventors, it was confirmed that when the melting heat value in a differential scanning calorimetry on polyethylene yarn satisfies the ratio range according to the present disclosure, it can exhibit excellent thermal properties in post-processing process such as dyeing, coating, and curing.

[0017] According to an embodiment of the present disclosure, there is provided a polyethylene yarn satisfying the following Equation 1:

[Equation 1]

$$0.05 \leq [(A-B)/A] \leq 0.35$$

[0018] In Equation 1, A is the melting heat value(ΔH_f, J/g) at a first temperature rise (1st run: heating from 50 °C to 180 °C at 10 °C/min) according to a differential scanning calorimetry on the polyethylene yarn.

[0019] In Equation 1, B is the melting heat value(ΔH_f, J/g) at a second temperature rise (2nd run: heating from 50 °C to 180 °C at 10 °C/min on the polyethylene yarn cooled to 50 °C after the first temperature rise) according to a differential scanning calorimetry on the polyethylene yarn.

[0020] In the differential scanning calorimetry, the first temperature rise (1st run) is measured while raising the temperature of the polyethylene yarn at a constant rate. In the first temperature rise, a peak caused by the thermal history of the polyethylene yarn is observed.

[0021] The polyethylene yarn completely melted in the first temperature rise is cooled, and then the second temperature rise (2nd run) is performed while raising the temperature again at a constant rate. In the second temperature rise, a peak caused by the inherent properties of the sample is observed.

[0022] The Equation 1 is a range of ratios calculated from the melting heat value(A) at the first temperature rise and the melting heat value(B) at the second temperature rise for the polyethylene yarn.

[0023] According to one embodiment, the polyethylene yarn preferably has a ratio of the melting heat value ([(A-B)/A]) of 0.05 to 0.35 according to Equation 1.

[0024] Specifically, the polyethylene yarn may have a ratio of the melting heat value according to Equation 1 of 0.05 or more, or 0.10 or more, or 0.15 or more; and 0.35 or less, or 0.30 or less, or 0.26 or less.

[0025] In order to exhibit excellent thermal properties according to the present disclosure, the polyethylene yarn preferably has a ratio of the melting heat value according to Equation 1 of 0.05 or more, or 0.10 or more, or 0.15 or more. However, if the ratio of the melting heat value is too large, mechanical properties of the yarn may be deteriorated, such as yarn breakage occurring during the drawing process. Therefore, the polyethylene yarn preferably has a ratio of the melting heat value according to Equation 1 of 0.35 or less, or 0.30 or less, or 0.26 or less.

[0026] Preferably, the polyethylene yarn may have a ratio of the melting heat value according to Equation 1 of 0.05 to 0.35, or 0.10 to 0.35, or 0.10 to 0.30, or 0.15 to 0.30, or 0.15 to 0.26.

[0027] As a non-limiting example, the first temperature rise and the second temperature rise may be performed by continuous operations under the following conditions using a conventional differential scanning calorimeter.

[0028] A polyethylene yarn sample was subjected to temperature rise (first temperature rise) from 50 °C to 180 °C at 10 °C/min; holding at 180 °C for 1 minute to 5 minutes; cooling from 180 °C to 50 °C at 200 °C/min; holding at 50 °C for 1 minute to 5 minutes; temperature rise (second temperature rise) from 50 °C to 180 °C at 10 °C/min; holding at 180 °C for 1 to 5 minutes; and cooling from 180 °C to 50 °C at 10 °C/min.

[0029] According to one embodiment, the polyethylene yarn may have a melting temperature (T_m) of 128 °C to 145 °C, or

129 °C to 145 °C, or 129 °C to 140 °C.

[0030] Preferably, the polyethylene yarn may have a melting temperature(T_m) of 130 °C to 145 °C, or 132 °C to 145 °C, or 132 °C to 140 °C at the first temperature rise.

[0031] Further, the polyethylene yarn can have a melting temperature(T_m) of 128 °C to 135 °C, or 129 °C to 135 °C, or 129 °C to 132 °C at the second temperature rise.

[0032] According to one embodiment, the polyethylene yarn may have a melt index (190 °C, load: 2.16 kgf) of 0.3 g/10min to 5.0 g/10min.

[0033] Specifically, the polyethylene yarn may have a melt index (190 °C, load: 2.16 kgf) of 0.3 g/10min or more, or 1.0 g/10min or more, or 1.5 g/10min or more, or 2.0 g/10min or more; and 5.0 g/10min or less, or 4.0 g/10min or less, or 3.0 g/10min or less.

[0034] In order to ensure appropriate productivity, the melt index of the polyethylene yarn is preferably 0.3 g/10 min or more, or 1.0 g/10 min or more, or 1.5 g/10 min or more, or 2.0 g/10 min or more. However, if the melt index is too high, the strength of the polyethylene yarn may be reduced. Therefore, the melt index of the polyethylene yarn is preferably 5.0 g/10 min or less, or 4.0 g/10 min or less, or 3.0 g/10 min or less.

[0035] Preferably, the polyethylene yarn may have a melt index of 0.3 g/10 min to 5.0 g/10 min, or 1.0 g/10 min to 5.0 g/10 min, or 1.0 g/10 min to 4.0 g/10 min, or 1.5 g/10 min to 4.0 g/10 min, or 1.5 g/10 min to 3.0 g/10 min, or 2.0 g/10 min to 3.0 g/10 min.

[0036] The melt index may be determined by a melt mass-flow rate(MFR) measurement method according to ISO 1133-1:2022 at a temperature of 190 °C under a load of 2.16 kgf.

[0037] According to one embodiment, the polyethylene yarn may have a crystallinity of 60% to 80%.

[0038] Specifically, the polyethylene yarn may have a crystallinity of 60% or more, or 65% or more, or 70% or more; and 80% or less or 75% or less.

[0039] In order to express appropriate mechanical properties, the polyethylene yarn preferably has a crystallinity of 60% or more, or 65% or more, or 70% or more. However, if the crystallinity is too high, processability may be deteriorated. Therefore, the polyethylene yarn preferably has a crystallinity of 80% or less or 75% or less.

[0040] Preferably, the polyethylene yarn may have a crystallinity of 60% to 80%, or 65% to 80%, or 65% to 75%.

[0041] According to one embodiment, the polyethylene yarn may have an L* value of 85.5 to 92.0.

[0042] The L* value is a lightness value in the L*a*b* (CIE LAB) color system measured using a spectrophotometer for a sample made from the polyethylene yarn. The L*a*b* (CIE LAB) color system is one of the methods of indicating color tones for color evaluation, and represents a color seen with the eye as a color space, which is established by the International Commission on Illumination (CIE). The L* value is an indicator of the tendency of lightness, and has a range of 0 to 100.

[0043] Specifically, the polyethylene yarn may have the L* value of 85.5 or more or 86.0 or more; and 92.0 or less or 91.5 or less. Preferably, the polyethylene yarn may have the L* value of 85.5 to 92.0, or 86.0 to 92.0, or 86.0 to 91.5. The L* value may be a value measured in a reflection mode on a sample of an appropriate size using a spectrophotometer.

[0044] As the polyethylene yarn meets the above properties, it can exhibit excellent thermal properties in post-processing process such as dyeing, coating, and curing. The polyethylene yarn can be used for manufacturing various products such as rope-like string-shaped products, industrial or medical protective equipment, airbags, bedding, and cooling materials.

[0045] According to another embodiment of the present disclosure, there is provided a method for manufacturing the polyethylene yarn, the method comprising the steps of:

providing a melt containing polyethylene having a weight average molecular weight(Mw) of 50,000 g/mol to 600,000 g/mol and a melt index (190 °C, load: 2.16 kgf) of 0.3 g/10 min to 5.0 g/10 min,
extruding the melt through a spinneret to obtain filaments,
cooling the filaments,
drawing a multi-filament composed of the cooled filaments, and
winding the drawn multi-filaments.
wherein the cooling is performed in a quenching zone having a plurality of cooling sections divided by the temperature of the sections, and the plurality of cooling sections are set to have a temperature gradient that gradually decreases toward a discharge part from an introduction part of the filaments.

[0046] FIG. 1 is a process diagram simplifying and showing a process of manufacturing polyethylene yarn according to an embodiment of the present disclosure.

[0047] Referring to FIG. 1, the method for manufacturing the polyethylene yarn may be performed by including a step of feeding a raw material containing polyethylene resin into an extruder 100 to provide a melt for spinning; a step of extruding the melt through a spinneret 200 to obtain filaments 11; a step of cooling the filaments 11 in a quenching zone 300; a step of drawing a multifilament 10, which is obtained by drawing the filaments 11 in an interlace 400, in a multi-stage drawing zone

500; and a step of winding the drawn multifilament with a winder 600.

[0048] Hereinafter, with reference to FIG. 1, each step that may be included in the method for manufacturing the polyethylene yarn will be described.

[0049] First, a step of feeding a raw material containing polyethylene resin to provide a melt for spinning is performed.

[0050] The polyethylene may have a weight average molecular weight(Mw) of 50,000 to 600,000 g/mol.

[0051] In order to ensure appropriate strength of the yarn, the weight average molecular weight(Mw) of the polyethylene is preferably 50,000 g/mol or more. However, if the molecular weight of the polyethylene is too large, overloading may be applied to the spinning device due to the high melt viscosity, which makes process control difficult, and results in deterioration of physical properties of the yarn. Therefore, the weight average molecular weight(Mw) of the polyethylene is preferably 600,000 g/mol or less.

[0052] Preferably, the weight average molecular weight(Mw) of the polyethylene may be 50,000 g/mol to 600,000 g/mol, or 100,000 g/mol to 500,000 g/mol, or 100,000 g/mol to 450,000 g/mol, or 150,000 g/mol to 450,000 g/mol, or 150,000 g/mol to 400,000 g/mol, or 200,000 g/mol to 400,000 g/mol, or 250,000 g/mol to 400,000 g/mol, or 300,000 g/mol to 400,000 g/mol.

[0053] After a polyethylene is completely dissolved in a solvent, the weight average molecular weight(Mw) can be determined by a gel permeation chromatography (GPC) under the following conditions.

- Analysis instrument: PL-GPC 220 system
- Column: 2 × PLGEL MIXED-B (7.5 × 300 mm)
- Solvent: trichlorobenzene(TCB) + 0.04 wt.% dibutylhydroxytoluene(BHT) (after drying with 0.1% $CaCl_2$)
- Injector, detection temperature: 160 °C
- Flow velocity: 1.0 mℓ/min
- Injection amount: 200 $\mu\ell$
- Standard sample: polystyrene

[0054] The polyethylene may have a melt index (190°C, load: 2.16 kgf) of 0.3 g/10 min to 5.0 g/10 min.

[0055] In order to ensure smooth flowability within the extruder 100, the melt index of the polyethylene is preferably 0.3 g/10 min or more or 0.5 g/10 min or more. However, if the melt index of the polyethylene is too high, it may be difficult to achieve high strength due to the relatively low molecular weight. Therefore, the melt index of the polyethylene is preferably 5.0 g/10 min or less, or 4.0 g/10 min or less, or 3.0 g/10 min or less.

[0056] Preferably, the melt index of the polyethylene may be 0.3 g/10 min to 5.0 g/10 min, or 0.3 g/10 min to 4.0 g/10 min, 0.3 g/10 min to 3.0 g/10 min, or 0.5 g/10 min to 3.0 g/10 min.

[0057] The melt index can be determined by the melt mass-flow rate (MFR) measurement method according to ISO 1133-1:2022 at a temperature of 190 °C under a load of 2.16 kgf.

[0058] Then, a step of extruding the melt through a spinneret to obtain filaments is performed. As a non-limiting example, a spinneret having 40 to 500 or 100 to 500 holes can be used in the step. The melt is extruded through the spinneret 200 while being conveyed by a screw (not shown) in an extruder 100.

[0059] The spinning step is preferably performed at a temperature of 250 to 315 °C or 280 to 310 °C.

[0060] In order to ensure the formation of the uniform melt and stable spinning, the temperature inside the extruder 100 and the spinneret 200 in the spinning step is preferably 250 °C or more. However, if the temperature in the spinning step is too high, thermal decomposition of the melt may occur, thereby making it difficult to achieve high strength. Therefore, the temperature inside the extruder 100 and the spinneret 200 in the spinning step is preferably 315 °C or less.

[0061] The L/D, which is a ratio of the hole length(L) to the hole diameter(D) of the spinneret 200, may be 3 to 40, or 5 to 30, or 5 to 20, or 10 to 20.

[0062] In order to prevent a die swell phenomenon from occurring during melt extrusion, the L/D is preferably 3 or more. However, if the L/D is too large, a nonuniform phenomenon of discharge due to pressure drop may occur along with a necking phenomenon of the melt passing through the spinneret 200. Therefore, the L/D is preferably 40 or less.

[0063] In consideration of processability and productivity, the spinning step is preferably performed so that the melt is extruded from the spinneret at a single hole discharge amount of 0.05 to 0.45 g/min and a discharge linear velocity of 0.3 to 5.0 cm/sec.

[0064] In the spinning step, if the draft ratio ($DR=V_1/V_0$) is too large, yarn breakage occurs frequently, which deteriorates the workability, and if the draft ratio is too small, orientation crystallization may not achieve sufficiently, which may deteriorate the dimensional stability of the filaments. Here, the V_0 is the discharge linear velocity of the melt (i.e., the average velocity until the melt vertically falls 1.25 m from the holes of the spinneret 200), and the V_1 is the spinning velocity (i.e., the linear velocity of the first godet roller GR1).

[0065] As the spinning velocity(V_1) is higher, the total draw ratio may be lower in the drawing process, which ultimately makes it more difficult to improve the strength of the yarn. Therefore, in order to ensure an appropriate spinning draft ratio, the discharge line velocity(V_0) is preferably 0.3 cm/sec or more. However, if the discharge linear velocity is too high, it is

difficult to apply a high draw ratio and thus, the discharge linear velocity(V_0) is preferably 5.0 cm/sec or less.

[0066] Specifically, the discharge linear velocity(V_0) may be 0.3 to 5.0 cm/sec, or 1.0 to 4.0 cm/sec, or 2.0 to 3.0 cm/sec.

[0067] Further, in order to ensure the discharge linear velocity of 0.3 to 5.0 cm/sec in the spinning step while meeting the requirement of a single yarn fineness of 10 denier or less, it is preferable that a relatively small single hole discharge amount (e.g., 0.05 to 0.45 g/min, or 0.1 to 0.40 g/min, or 0.15 to 0.35 g/min) is applied in the spinning step.

[0068] Then, a step of cooling the filaments is performed.

[0069] As the melt discharges from the holes of the spinneret 200, solidification of the melt begins due to a difference between a spinning temperature and room temperature to form filaments in a semi-solidified state. In the present specification, both the filaments in a semi-solidified state and completely solidified filaments are collectively referred to as "filaments".

[0070] The plurality of filaments 11 formed as the melt is discharged from the holes of the spinneret 200 are cooled in a quenching zone 300 to be completely solidified.

[0071] According to one embodiment, the cooling is performed in a quenching zone 300 having a plurality of cooling sections divided by the temperature of the sections, and the plurality of cooling sections can be set to have a temperature gradient that gradually decreases toward a discharge part from an introduction part of the filaments.

[0072] Cooling of the filaments is performed in the quenching zone 300 having a plurality of cooling sections set to have the temperature gradient, so that a polyethylene yarn satisfying the thermal properties according to the Equation 1 can be provided. In addition, by performing the cooling as described above, a polyethylene yarn having a higher crystallinity and a better appearance can be provided.

[0073] According to one embodiment, the quenching zone can be advantageous for the above-mentioned effects when it has from two to five cooling sections.

[0074] Preferably, the plurality of cooling sections may be set to have a temperature gradient that gradually decreases toward the discharge part from the introduction part of the filaments in a temperature range of 15 °C to 80 °C.

[0075] In order to prevent yarn breakage in the drawing process due to overcooling of the filaments, the filaments 11 are preferably cooled at a temperature of 15 °C or more or 20 °C or more. However, if the filaments are not sufficiently cooled, the fineness deviation may increase due to solidification unevenness, and yarn breakage may occur in the drawing process. Therefore, the filaments 11 are preferably cooled to 80 °C or less or 75 °C or less.

[0076] FIGs. 2 to 4 each show a schematic configuration of a quenching zone 300 according to an embodiment of the present disclosure in the process diagram of FIG. 1.

[0077] In FIG. 2, the quenching zone 300 has a first cooling section 310 and a second cooling section 320 disposed toward the discharge part from the introduction part of the filaments. According to one embodiment, the first cooling section 310 may be set to a temperature selected in the range of 45 °C to 80 °C, and the second cooling section 320 may be set to a temperature selected in the range of 15 °C to 40 °C.

[0078] In FIG. 3, the quenching zone 300 comprises a first cooling section 310, a second cooling section 320, and a third cooling section 330 which are disposed toward the discharge part from the introduction part of the filaments. According to one embodiment, the first cooling section 310 may be set to a temperature selected in the range of 45 °C to 80 °C, the second cooling section 320 may be set to a temperature selected in the range of 30 °C to 50 °C, and the third cooling section 330 may be set to a temperature selected in the range of 15 °C to 30 °C.

[0079] In FIG. 4, the quenching zone 300 comprises a first cooling section 310, a second cooling section 320, a third cooling section 330, and a fourth cooling section 340 which are disposed toward the discharge part from the introduction part of the filaments. According to one embodiment, the first cooling section 310 may be set to a temperature selected from a range of 45 °C to 80 °C, the second cooling section 320 may be set to a temperature selected from a range of 35 °C to 55 °C, the third cooling section 330 may be set to a temperature selected from a range of 20 °C to 40 °C, and the fourth cooling section 340 may be set to a temperature selected from a range of 15 °C to 25 °C.

[0080] Apart from the temperature setting for the cooling sections, cooling wind may be supplied to the plurality of cooling sections.

[0081] According to one embodiment, the wind velocity of the cooling wind may be set to have a wind velocity gradient that decreases toward the discharge part from the introduction part of the filaments.

[0082] Preferably, the plurality of cooling sections may be set to have a wind velocity gradient of the cooling wind that decreases toward the discharge part from the introduction part of the filaments in a wind velocity range of 0.1 m/s to 3.0 m/s. By imparting the wind velocity gradient of the cooling wind, a polyethylene yarn having a smoother surface can be obtained.

[0083] The cooled and completely solidified filaments are interlaced by an interlacer 400 to provide a multifilament 10.

[0084] Optionally, the method may further include applying an emulsion to the filaments using an oil roller OR or an oil jet before forming the multifilament 10. The application of the oil may be performed in a metered oiling manner. The application of the oil may be performed between the godet rollers and/or between the last godet roller and the winder 600 in a subsequent drawing step.

[0085] Then, a step of drawing the multifilament composed of the cooled filaments is performed.

[0086] According to one embodiment, the method for manufacturing the polyethylene yarn follows a process of sequentially transfering the multifilament 10, which is obtained by melt spinning, to a multi-stage drawing zone 500 including a plurality of godet rollers without separately winding the multifilament, and then directly drawing it. This manufacturing method is distinguished from a conventional two-stage process of winding the undrawn yarn formed by melt spinning and then drawing the undrawn yarn at a high draw ratio under high temperature.

[0087] In order to ensure that the polyethylene yarn finally obtained has high strength, the drawing step must be precisely controlled using a multi-stage drawing zone 500 including a plurality of godet rollers.

[0088] For this purpose, the drawing step is preferably performed in a multi-stage drawing zone 500 including two or more stages, or two to ten stages, or two to eight stages, or two to six stages of godet rollers (GR1, ..., GRn).

[0089] That is, the drawing step may be advantageous in obtaining a polyethylene yarn having excellent dimensional stability and high strength when it is performed in a multi-stage drawing zone equipped with two or more stages of godet rollers. However, if the number of godet rollers in the multi-stage drawing zone is too large, the polyethylene yarn finally obtained may not have the desired properties, or the efficiency of the overall process may be reduced. Therefore, the drawing step is preferably performed in a multi-stage drawing zone equipped with 10 or less stages, 8 or less stages, or 6 or less stages of godet rollers.

[0090] In order to ensure that sufficient drawing can be performed in the drawing step, the temperature of the plurality of godet rollers included in the multi-stage drawing zone 500 may be set to 40 to 140 °C.

[0091] For example, the temperature of the first godet roller GR1 among the plurality of godet rollers may be set to 40 to 80 °C, and the temperature of the last godet roller GRn may be set to 110 to 140 °C. Among the plurality of godet rollers, the temperatures of the remaining godet rollers GR2 to GRn-1, excluding the first and last godet rollers GR1 and GRn, may be set to be equal to or higher than the temperature of the godet roller located immediately before the corresponding godet rollers. If necessary, any godet roller may be set to a temperature lower than the temperature of the godet roller located immediately before the corresponding godet roller.

[0092] The total draw ratio of the multifilament in the multi-stage drawing zone 500 is a factor determined by the linear velocity (mpm) of the first godet roller GR1 and the linear velocity (mpm) of the last godet roller GRn. That is, the total draw ratio means a value obtained by dividing the linear velocity of the last godet roller GRn among the godet rollers provided in the multi-stage drawing zone 500 by the linear velocity of the first godet roller GR1.

[0093] When the linear velocity of the first godet roller GR1 is determined, the linear velocity of the remaining godet rollers can be determined so that a total draw ratio of 4 to 15 times can be applied to the multifilament 10 in the multi-stage drawing zone 500.

[0094] Drawing and heat-setting of the multifilament are performed through the drawing step.

[0095] Unlike the method in which heat-setting is roughly performed using hot air, etc., in the multi-stage drawing zone 500 of the drawing step, the multifilament is drawn by directly contacting the plurality of godet rollers, so that heat-setting can be precisely performed.

[0096] Then, a step of winding the drawn multifilament is performed. In the drawing step, the multi-stage drawn multifilament is wound by a winder 600 to obtain polyethylene yarn.

[ADVANTAGEOUS EFFECTS]

[0097] According to the present disclosure, a polyethylene yarn having excellent thermal properties and a method capable of efficiently manufacturing the polyethylene yarn are provided.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0098]

FIG. 1 is a schematic process diagram showing a process for manufacturing polyethylene yarn according to an embodiment of the present disclosure.

FIGs. 2 to 4 show a schematic configuration of a quenching zone according to an embodiment of the present disclosure in the process diagram of FIG. 1, respectively.

FIGs. 5 to 7 are temperature-rising DSC curves [X-axis = temperature (°C); Y-axis = heat absorption value (mW)] obtained by differential scanning calorimetry on polyethylene yarn according to Examples and Comparative Examples of the present disclosure.

<Description of Reference Numerals>

[0099]

100:	extruder	200:	spinneret
300:	quenching zone	310:	first cooling section
320:	second cooling section	330:	third cooling section
340:	fourth cooling section	11:	filament
10:	multifilament	OR:	oil roller
400:	interlacing part	500:	multi-stage drawing zone
GR1:	first godet roller	GRn:	last godet roller
600:	winder		

[DETAILED DESCRIPTION OF THE EMBODIMENTS]

[0100] Hereinafter, preferred Examples are provided for better understanding of the invention. However, these Examples are for illustrative purposes only, and the invention is not intended to be limited by these Examples.

Example 1

[0101] A polyethylene yarn containing 200 filaments and having a total fineness of 400 denier was manufactured by using the device shown in FIG. 1.

[0102] Specifically, polyethylene chips having a weight average molecular weight (Mw) of 340,000 g/mol and a melt index (190 °C, load: 2.16 kgf) of 1.8 g/10 min were fed into an extruder 100. The chips fed into the extruder 100 were melted to prepare a melt for spinning.

[0103] The melt was extruded through a spinneret 200 having 200 holes.

[0104] The filaments 11 formed while being discharged from the spinneret 200 were cooled in a quenching zone 300 having a configuration according to FIG. 4.

[0105] The quenching zone 300 comprises a first cooling section 310, a second cooling section 320, a third cooling section 330, and a fourth cooling section 340 disposed toward the discharge part from the introduction part of the filaments.

[0106] The first cooling section 310 was set to a temperature of 45 °C; the second cooling section 320 was set to a temperature of 35 °C; the third cooling section 330 was set to a temperature of 25 °C; and the fourth cooling section 340 was set to a temperature of 15 °C.

[0107] Cooling wind was supplied to the cooling sections. The wind velocity of the cooling wind was set to have a wind velocity gradient that decreased toward the discharge part from the introduction part of the filaments in a wind velocity range of 0.1 m/s to 3.0 m/s.

[0108] The cooled filaments 11 were interlaced into a multifilament 10 by an interlacer 400 and continuously moved to a multi-stage drawing zone 500 equipped with 4 stages of godet rollers GR1-GR8. Continuously, in the multi-stage drawing zone 500, the multifilament 10 was directly contacted with the godet rollers to be drawn and heat-set at a total drawing ratio of 8 times and a relaxation ratio of 4%. The temperature range of the godet rollers was set to 80 to 130 °C.

[0109] The multi-stage drawn multifilament was wound on a winder 600 under a winding tension of 0.8 g/d to obtain a polyethylene yarn.

Example 2

[0110] A polyethylene yarn was manufactured in the same manner as in Example 1, except that drawing was performed at a total draw ratio of 4 times in the multi-stage drawing zone 500.

Example 3

[0111] A polyethylene yarn was manufactured in the same manner as in Example 1, except that the filaments were drawn at a total draw ratio of 12 times in the multi-stage drawing zone 500.

Example 4

[0112] A polyethylene yarn was manufactured in the same manner as in Example 1, except that cooling of the filaments 11 was performed in the quenching zone 300 having the configuration according to FIG. 2, and drawing was performed in the multi-stage drawing zone 500 equipped with two stages of godet rollers GR1-GR4.

[0113] The quenching zone 300 comprises a first cooling section 310 and a second cooling section 320m which are disposed toward the discharge part from the introduction part of the filaments; the first cooling section 310 was set to a

temperature of 45 °C; and the second cooling section 320 was set to a temperature of 25 °C.

Example 5

[0114] A polyethylene yarn was manufactured in the same manner as in Example 1, except that polyethylene chips having a weight average molecular weight(Mw) of 340,000 g/mol and a melt index of 0.5 g/10 min (190 °C, load: 2.16 kgf) were used.

Comparative Example 1

[0115] A polyethylene yarn was manufactured in the same manner as in Example 1, except that cooling of the filaments was performed in a quenching zone consisting of a single cooling section instead of the quenching zone having the configuration according to FIG. 4. At this time, the quenching zone was set to a temperature of 45 °C.

Comparative Example 2

[0116] A polyethylene yarn was manufactured in the same manner as in Example 2, except that polyethylene chips having a weight average molecular weight(Mw) of 200,000 g/mol and a melt index of 7.0 g/10 min (190 °C, load: 2.16 kgf) were used.

Comparative Example 3

[0117] A polyethylene yarn was manufactured in the same manner as in Example 4, except that polyethylene chips having a weight average molecular weight(Mw) of 200,000 g/mol and a melt index (190 °C, load: 2.16 kgf) of 7.0 g/10 min were used.

Test Example

[0118] The polyethylene yarns manufactured in Examples and Comparative Examples were tested by the following methods, and the results are shown in Table 1 below.

(1) Crystallinity of polyethylene yarn

[0119] The crystallinity of the polyethylene yarn was measured by using an X-ray diffraction analyzer utilizing an X-ray source. Specifically, the polyethylene yarn was cut to prepare a sample with a length of 2.5 cm, and the sample was fixed to a sample holder of the X-ray diffractometer, and the measurement was performed under the following conditions.

i) Experimental equipment: Empyrean (Malvern Panalytical Ltd)
ii) X-ray source: Cu-Ka (1.54 Å), 45 kV, 20 mA
iii) Incident beam path

- Filter: Beta-filter Nickel 0.02 mm
- Slit: AS 1°, DS 1/2°, SS : 0.04 rad
- Mask: 10 mm

iv) Diffracted beam path

- Detector: PIXcel3D 2X2 (area detector)
- Slit: AS 5.0 mm, SS: 0.04 rad

v) Scan range : 10° ~ 32°
vi) Step size: 0.1°
vii) Beam direction: Reflection
viii) Background Method: Constant Background
ix) Standard Specimen: 3000 Denier
x) Apparent crystallite size(ACS) : estimated from the half-height of the peak (110) plane, (200) plane using the Scherrer equation.

-

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

- λ: X-ray wavelength, 0.154nm
- β: FWHM
- Θ: bragg angle (max. peak)
- Scherrer constant K = 0.89

xi) Crystallinity(Xc) : Constant background method

(2) Melting temperature and melting heat of polyethylene yarn

[0120] Using a differential scanning calorimeter (model name: DSC7, manufacturer: Perkin Elmer), the melting temperature and melting heat of polyethylene yarn samples were measured continuously under the conditions below at the first and second temperature rises. Then, the value of Equation 1 was calculated from the melting heat values at the first and second temperature rises.

[0121] Temperature rise (first temperature rise) from 50 °C to 180 °C at 10 °C/min; holding at 180 °C for 1 minute to 5 minutes; cooling from 180 °C to 50 °C at 200 °C/min; holding at 50 °C for 1 minute to 5 minutes; temperature rise (second temperature rise) from 50 °C to 180 °C at 10 °C/min; holding at 180 °C for 1 to 5 minutes; and cooling from 180 °C to 50 °C at 10 °C/min.

[0122] FIG. 5 is a DSC curve [X-axis = temperature(°C); Y-axis = heat absorption value (mW)] of the first and second temperature rises on the polyethylene yarn according to Example 1. FIG. 6 is a DSC curve of the first and second temperature rises on the polyethylene yarn according to Example 2. FIG. 7 is a DSC curve of the first and second temperature rises on the polyethylene yarn according to Comparative Example 2.

(3) Color of polyethylene yarn

[0123] The lightness(L*) value of the polyethylene yarn samples according to the L*a*b* (CIE LAB) color system was measured using a spectrophotometer (model name: Ci7860, manufacturer: X-Rite). A sample having a size of 63.5 mm x 12.7 mm x 3.2 mm in ASTM D256 standard was prepared, and measured three times in a reflection mode, after which the average value was recorded.

(4) Dry heat shrinkage rate

[0124] A polyethylene yarn sample was left in a constant temperature and humidity room at 25°C and 65% relative humidity for 24 hours. The sample was heat-shrunk under no tension at 150°C for 30 minutes, and then left again in the constant temperature and humidity room for 24 hours. The length of the sample before and after shrinkage was measured, and the dry heat shrinkage rate was calculated according to the following Equation.

$$\text{Dry heat shrinkage rate (\%)} = [(L_0-L_1)/L_0] \times 100$$

L_0: Length of the sample before heat shrinkage after leaving it in a constant temperature and humidity chamber at 25 °C and 65% relative humidity for 24 hours

L_1: Length of the sample after the sample after heat shrinkage was left in a constant temperature and humidity chamber at 25 °C and 65% relative humidity for 24 hours

[Table 1]

Yarn	MI (g/10min)	Crystallinity (%)	Melting temp. at 1st temp. rise (°C)	Melting temp. at 2nd temp. rise (°C)	(A-B)/A	L*	Dry heat shrinkage rate (%)
Example 1	2.4	70	135	129	0.185	88	3.0

(continued)

Yarn	MI (g/10min)	Crystallinity (%)	Melting temp. at 1st temp. rise (°C)	Melting temp. at 2nd temp. rise (°C)	(A-B)/A	L*	Dry heat shrinkage rate (%)
Example 2	2.4	70	135	129	0.185	88	2.9
Example 3	2.1	73	140	130	0.253	89	2.5
Example 4	2.7	70	133	129	0.170	86	3.2
Example 5	2.1	75	139	130	0.253	91	2.5
Comparative Example 1	2.4	62	130	129	0.049	87	3.9
Comparative Example 2	11.8	57	127	127	0.01	87	4.3
Comparative Example 3	12.1	55	128	127	0.03	86	4.3

[0125] Referring to Table 1, it was confirmed that the polyethylene yarns according to Examples exhibit lower dry heat shrinkage rates while having generally higher L* values than the polyethylene yarns according to Comparative Examples, thus exhibiting superior thermal properties.

Claims

1. A polyethylene yarn satisfying the following Equation 1:

$$[\text{Equation 1}]$$

$$0.05 \leq [(A-B)/A] \leq 0.35$$

in Equation 1,

A is the melting heat value(ΔH_f, J/g) at a first temperature rise (1st run: heating from 50 °C to 180 °C at 10 °C/min) according to a differential scanning calorimetry on the polyethylene yarn, and
B is the melting heat value(ΔH_f, J/g) at a second temperature rise (2nd run: heating from 50 °C to 180 °C at 10 °C/min on the polyethylene yarn cooled to 50 °C after the first temperature rise) according to a differential scanning calorimetry on the polyethylene yarn.

2. The polyethylene yarn according to claim 1, wherein the polyethylene yarn has a melting temperature (T_m) of 128 °C to 145 °C.

3. The polyethylene yarn according to claim 1, wherein the polyethylene yarn has a melting temperature (T_m) of 130 °C to 145 °C at the first temperature rise, and a melting temperature (T_m) of 128 °C to 135 °C at the second temperature rise.

4. The polyethylene yarn according to claim 1, wherein the polyethylene yarn has a melt index (190 °C, load: 2.16 kgf) of 0.3 g/10 min to 5.0 g/10 min.

5. The polyethylene yarn according to claim 1, wherein the polyethylene yarn has a crystallinity of 60% to 80%.

6. The polyethylene yarn according to claim 1, wherein the polyethylene yarn has an L* value (lightness value in the L*a*b* (CIE LAB) color system measured using a spectrophotometer on a sample made from the polyethylene yarn) of 85.5 to 92.0.

7. A method for manufacturing the polyethylene yarn of claim 1, the method comprising the steps of:

providing a melt containing polyethylene having a weight average molecular weight(Mw) of 50,000 g/mol to 600,000 g/mol and a melt index (190 °C, load: 2.16 kgf) of 0.3 g/10 min to 5.0 g/10 min,

extruding the melt through a spinneret to obtain filaments,
cooling the filaments,
drawing a multi-filament composed of the cooled filaments, and
winding the drawn multi-filaments.
wherein the cooling is performed in a quenching zone having a plurality of cooling sections divided by the temperature of the sections, and the plurality of cooling sections are set to have a temperature gradient that gradually decreases toward a discharge part from an introduction part of the filaments.

8. The method for manufacturing the polyethylene yarn according to claim 7, wherein the plurality of cooling sections are set to have a temperature gradient that gradually decreases toward the discharge part from the introduction part of the filaments in a temperature range of 15 °C to 80 °C.

9. The method for manufacturing the polyethylene yarn according to claim 7, wherein the quenching zone has two to five cooling sections.

10. The method for manufacturing the polyethylene yarn according to claim 7, wherein:

the quenching zone has first and second cooling sections disposed toward the discharge part from the introduction part of the filaments, and
the first cooling section is set to a temperature selected in the range of 45 °C to 80 °C, and the second cooling section is set to a temperature selected in the range of 15 °C to 40 °C.

11. The method for manufacturing the polyethylene yarn according to claim 7, wherein:

the quenching zone comprises first to third cooling sections disposed toward the discharge part from the introduction part of the filaments, and
the first cooling section is set to a temperature selected in the range of 45 °C to 80 °C, the second cooling section is set to a temperature selected in the range of 30 °C to 50 °C, and the third cooling section is set to a temperature selected in the range of 15 °C to 30 °C.

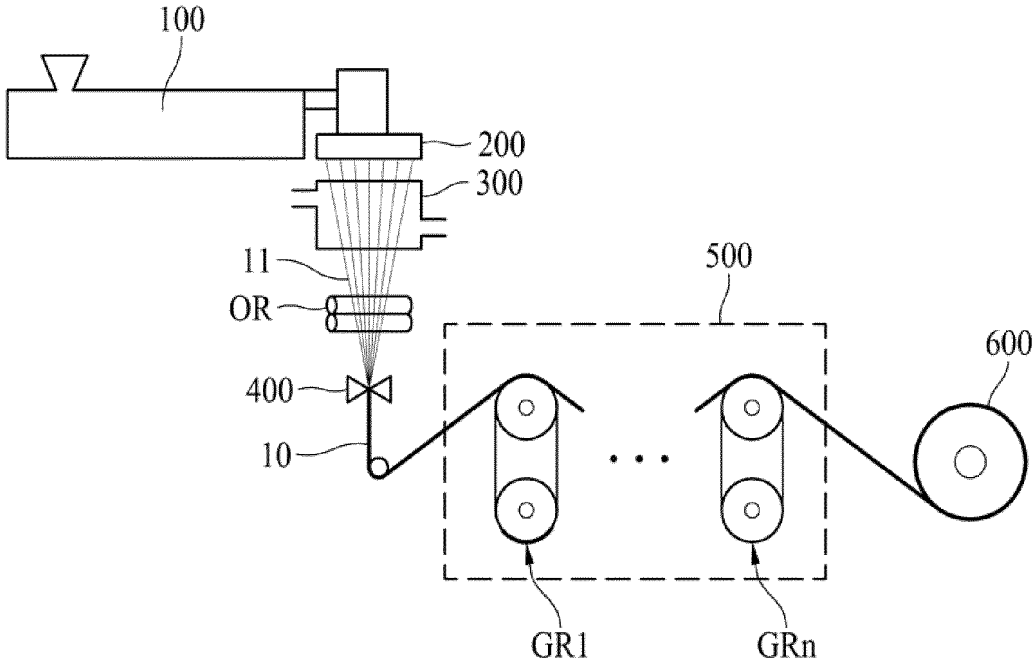
12. The method for manufacturing the polyethylene yarn according to claim 7, wherein:

the quenching zone comprises first to fourth cooling sections disposed toward the discharge part from the introduction part of the filaments, and
the first cooling section is set to a temperature selected in the range of 45 °C to 80 °C, the second cooling section is set to a temperature selected in the range of 35 °C to 55 °C, the third cooling section is set to a temperature selected in the range of 20 °C to 40 °C, and the fourth cooling section is set to a temperature selected in the range of 15 °C to 25 °C.

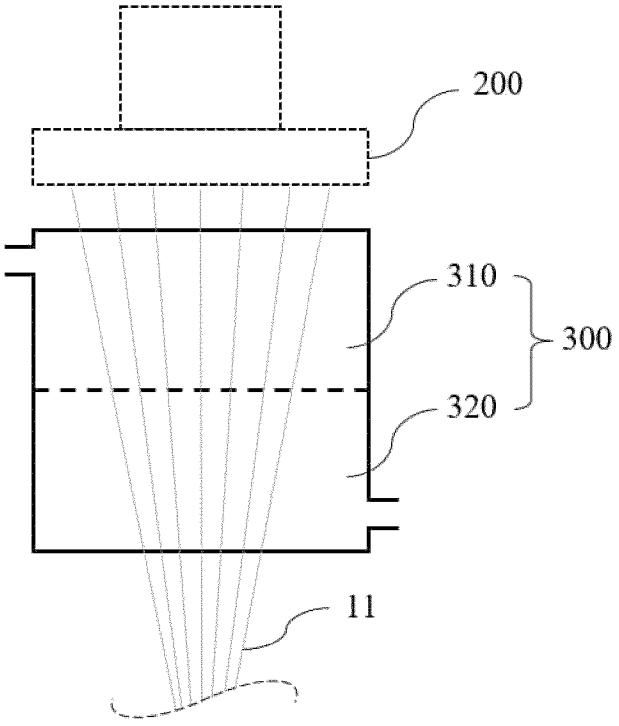
13. The method for manufacturing the polyethylene yarn according to claim 7, wherein:

cooling air is supplied to the plurality of cooling sections, and
the wind velocity of the cooling air is set to have a wind velocity gradient that decreases toward the discharge part from the introduction part of the filaments.

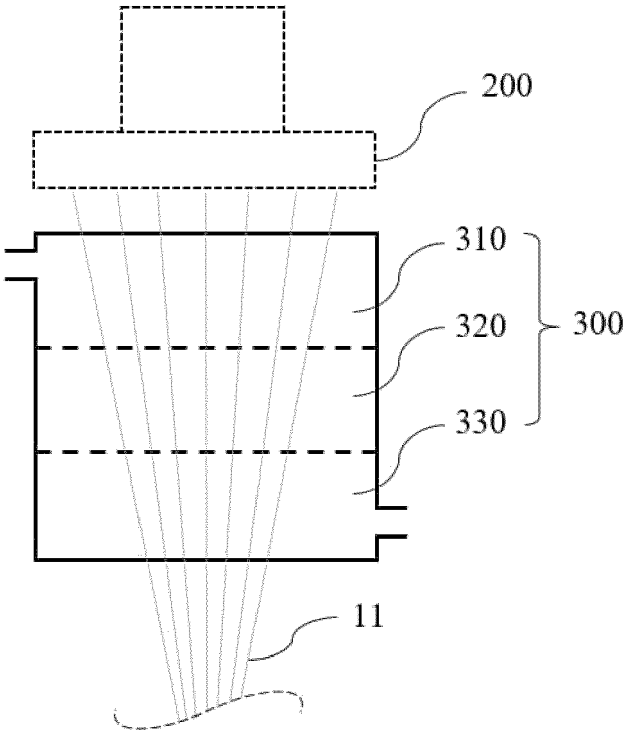
【FIG. 1】



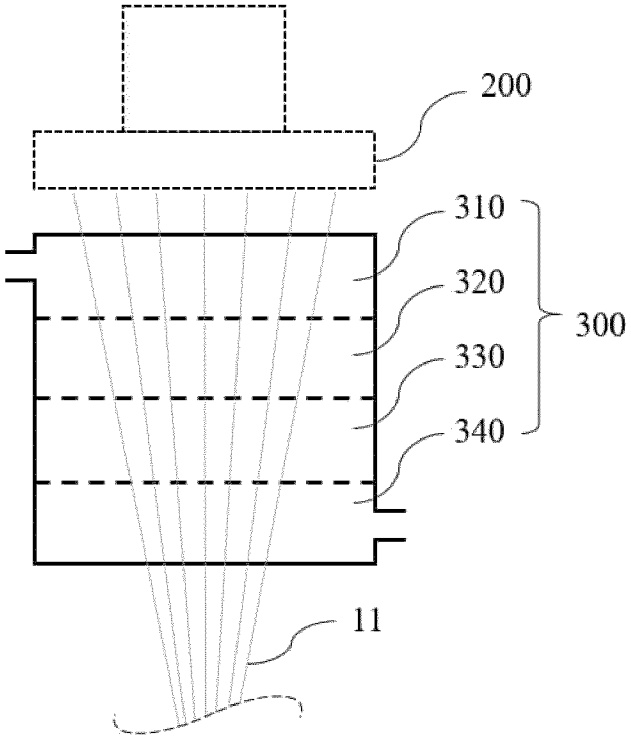
【FIG. 2】



【FIG. 3】

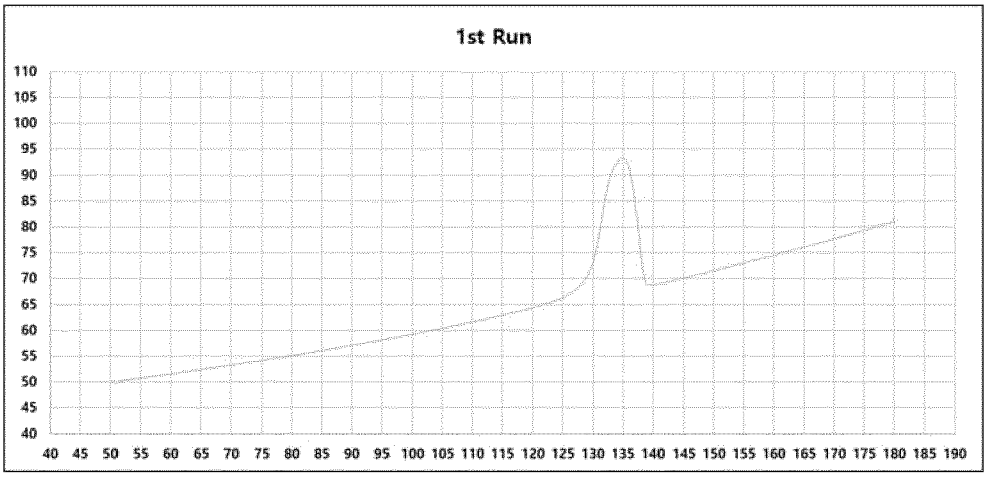


【FIG. 4】

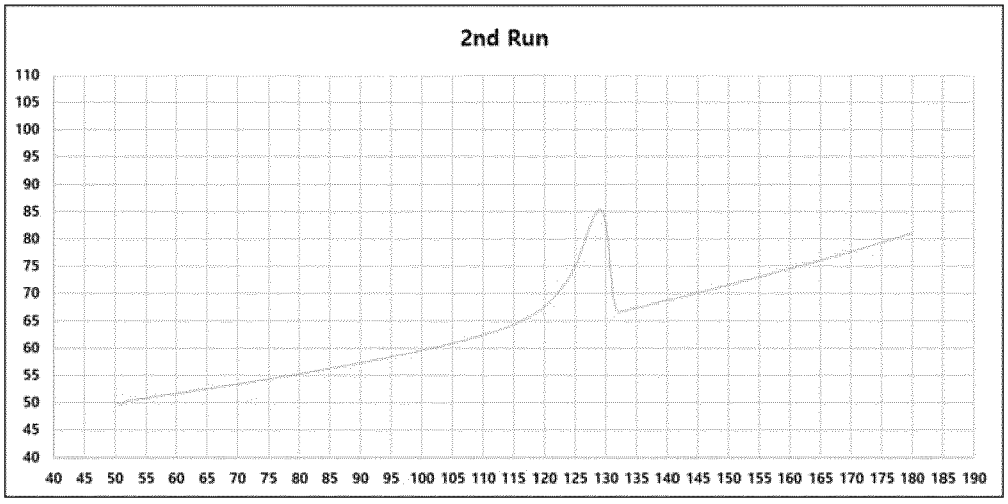


【FIG. 5】

(a)

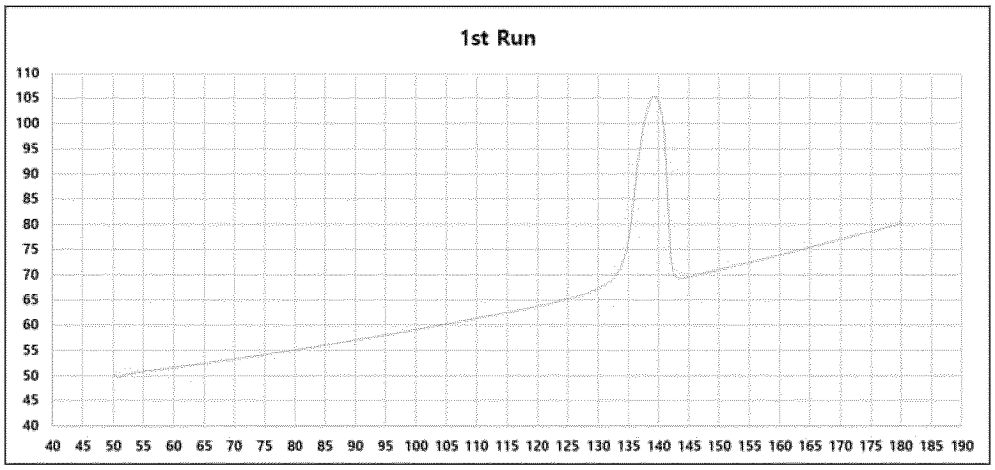

1st Run
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190

(b)

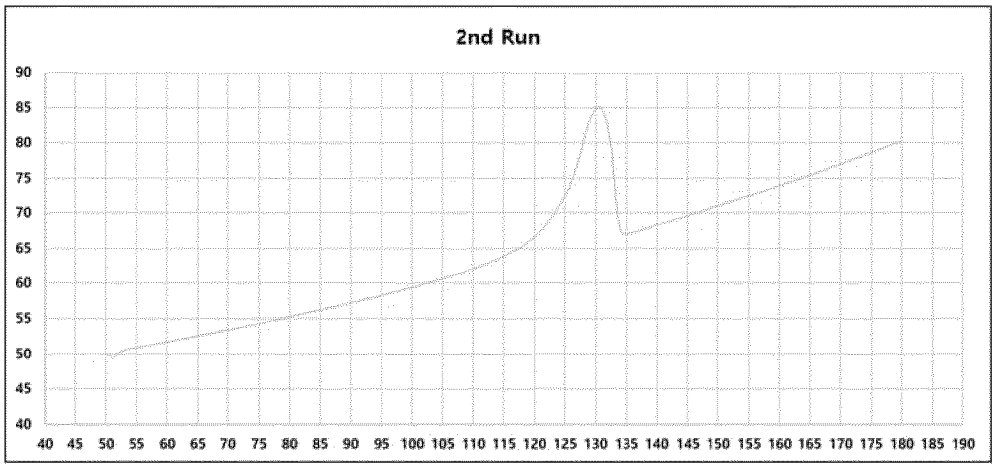

2nd Run
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190

【FIG. 6】

(a)


1st Run
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190

(b)


2nd Run
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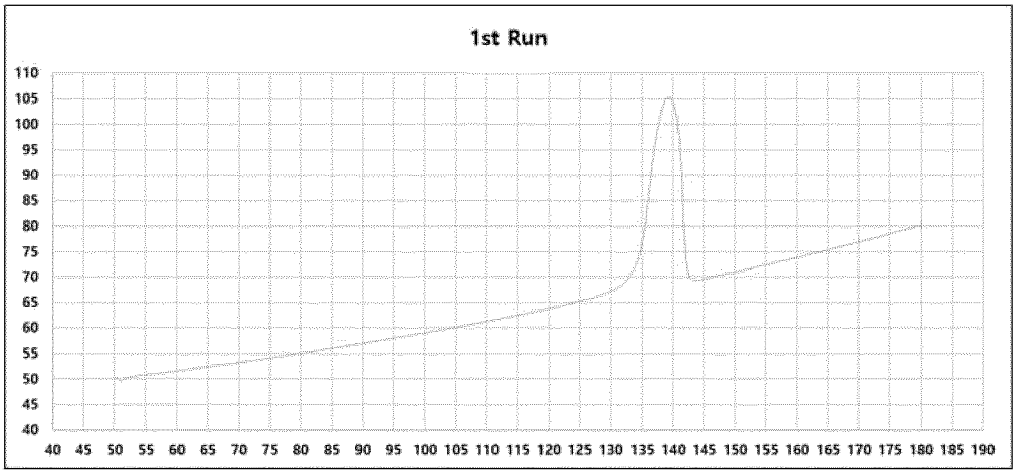
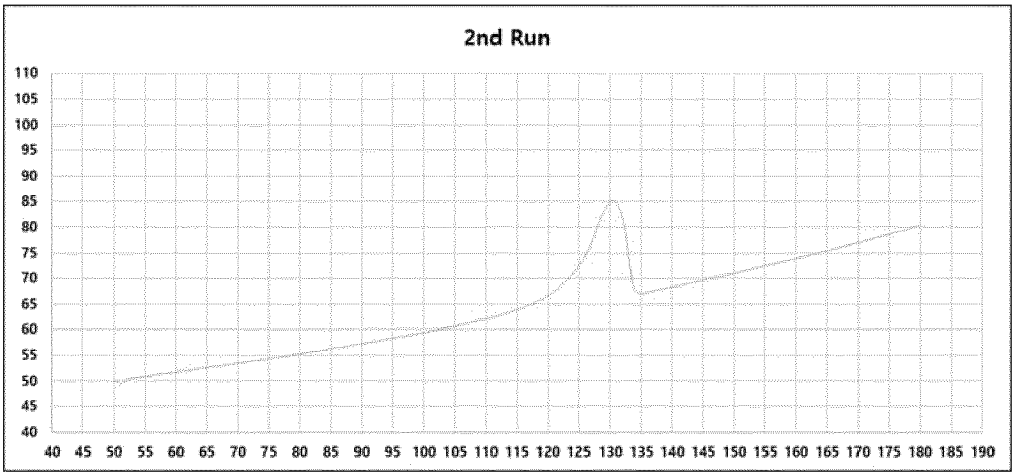
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190

【FIG. 7】

(a)


1st Run
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190

(b)


2nd Run
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2023/015055

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/04(2006.01)i; **D01D 5/088**(2006.01)i; **D01D 5/098**(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)

D01F 6/04(2006.01); C08F 210/02(2006.01); D01D 10/02(2006.01); D01D 5/088(2006.01); D01D 5/092(2006.01); D02G 3/00(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 폴리에틸렌 원사 (polyethylene yarn), 용융열 (heat of fusion), 중량 평균 분자량 (weight average molecular weight), 용융지수 (melting index)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021-132972 A1 (KOLON INDUSTRIES, INC.) 01 July 2021 (2021-07-01) See claims 1-18.	1-6
Y		7-13
Y	KR 10-1996-0006931 B1 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 25 May 1996 (1996-05-25) See paragraphs [0002]-[0033]; and figures 1-2.	7-13
A	JP 2020-016007 A (ASAHI KASEI CORP.) 30 January 2020 (2020-01-30) See entire document.	1-13
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A	US 5736244 A (KAVESH, S. et al.) 07 April 1998 (1998-04-07) See entire document.	1-13

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

* Special categories of cited documents:
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 January 2024	**15 January 2024**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2023/015055

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