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(72) Inventors:
• **MOKUDAI, Haruki**
Tokyo 103-8552 (JP)
• **FURUKAWA, Wataru**
Tokyo 103-8552 (JP)
• **MASAKI, Takashi**
Tokyo 103-8552 (JP)
• **SUZUKI, Yoshinori**
Tokyo 103-8552 (JP)

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(74) Representative: **Hoefer & Partner Patentanwälte
mbB**
Pilgersheimer Straße 20
81543 München (DE)

(71) Applicant: **Kureha Corporation**
Chuo-ku
Tokyo 103-8552 (JP)

(54) **MONOFILAMENT AND MANUFACTURING METHOD THEREFOR**

(57) To provide a monofilament of polyamide 4 (PA4) having high tensile characteristics even when the monofilament is knotted. A monofilament of PA4, in a scattering vector in a range of 0.02 nm⁻¹ or greater and 0.04 nm⁻¹ or less measured by small-angle X-ray scattering, the

monofilament having an average value of a ratio I2/I1 of a normalized scattering intensity I2 in an equatorial direction to a normalized scattering intensity I1 in a meridional direction of 5 or less. A birefringence of the monofilament is 50 × 10⁻³ or greater.

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Description**TECHNICAL FIELD**

[0001] The present invention relates to a monofilament and a manufacturing method therefor.

BACKGROUND ART

[0002] Practical use of polyamide 4 (hereinafter, also referred to as "PA4") as a bioplastic has been expected, and a large number of spinning methods therefor has been studied. One of the characteristics required for a monofilament of PA4 is having a high tensile strength. Known spinning methods for manufacturing monofilaments of such a PA4 having a high tensile strength include a solution spinning method using formic acid (e.g., see Patent Document 1), a gel spinning method using an ionic liquid, and a melt spinning method using an inorganic salt (e.g., see Patent Document 2).

Citation List**Patent Literature**

[0003]

Patent Document 1: JP 2019-137934 A

Patent Document 2: WO 2012/157576

SUMMARY OF INVENTION**TECHNICAL PROBLEM**

[0004] A monofilament is thought to be used, typically, in a state in which the monofilament is knotted. Thus, for a monofilament for such use, exhibition of high tensile characteristics is required when the monofilament is knotted. However, the known spinning methods described above have room for consideration from the viewpoints of suppressing occurrence of a void in a monofilament of PA4 and enhancing tensile characteristics when the monofilament is knotted.

[0005] In one aspect, an object of the present invention is to provide a monofilament of PA4 exhibiting high tensile characteristics even when the monofilament is knotted.

SOLUTION TO PROBLEM

[0006] To solve the problems described above, a monofilament according to one aspect of the present invention is a monofilament of polyamide 4, in a scattering vector in a range of 0.02 nm^{-1} or greater and 0.04 nm^{-1} or less measured by small-angle X-ray scattering, the monofilament having an average value of a ratio I_2/I_1 of a normalized scattering intensity I_2 in an equatorial direction to a normalized scattering intensity I_1 in a meridian direction of 5 or less, and a birefringence of the monofilament being 50×10^{-3} or greater.

[0007] Furthermore, to solve the problems described above, a method for manufacturing the monofilament according to one aspect of the present invention is a method for manufacturing a monofilament of polyamide 4 by drawing an un-drawn monofilament of polyamide 4. The method includes: a first drawing of drawing an un-drawn monofilament of polyamide 4 by dry heat drawing at a drawing temperature of 40°C or higher and a drawing ratio of 2.5 times or greater and 3.5 times or less; and a second drawing of drawing a primary drawn monofilament of the polyamide 4 produced in the first drawing by wet heat drawing at a drawing temperature of 80°C or higher and 120°C or lower and a specific drawing ratio. The specific drawing ratio is a drawing ratio that makes a total drawing ratio 3.5 times or greater, the total drawing ratio being a drawing ratio of the un-drawn monofilament caused by both the first and the second drawing (in a case where the total drawing ratio is 3.5 times, the drawing ratio in the first drawing is less than 3.5 times).

ADVANTAGEOUS EFFECTS OF INVENTION

[0008] According to an aspect of the present invention, a monofilament of PA4 exhibiting high tensile characteristics even when the monofilament is knotted can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

FIG. 1 is a photograph of a two-dimensional image of small-angle X-ray scattering (SAXS) of a monofilament of Example 1 of an embodiment of the present invention.

FIG. 2 is a photograph of a two-dimensional image of small-angle X-ray scattering (SAXS) of a monofilament of Comparative Example 1 of an embodiment of the present invention.

DESCRIPTION OF EMBODIMENTS

Monofilament

Polyamide 4

The monofilament of an embodiment of the present invention is substantially made of polyamide 4 (PA4). The PA4 is a polymer compound containing a structural unit represented by Formula (1) below. In the formula, x is 4.

[Chemical Formula 1]



In an embodiment of the present invention, a polymer compound constituting a structure of the monofilament may be PA4 alone. In an embodiment of the present invention, an additional component besides the PA4 may be further contained in a range where the effects of the present embodiment can be provided. The additional component may be one or more kinds, examples of which include a reinforcing agent, a plasticizer, a lubricant, and a stabilizer. The additional component may contain a polymer compound other than the PA4. The additional component is appropriately used in an amount that further exhibits the effects of the additional component. Thus, the monofilament of an embodiment of the present invention is a monofilament of the PA4.

Scattering Intensity Ratio of Small-Angle X-Ray Scattering

The monofilament of an embodiment of the present invention has a specific ratio of scattering intensities measured by small-angle X-ray scattering (SAXS) method. That is, in a scattering vector q in a range of 0.02 nm^{-1} or greater and 0.04 nm^{-1} or less as measured by small-angle X-ray scattering, the monofilament has an average value of a ratio I_2/I_1 of a normalized scattering intensity I_2 in an equatorial direction to a normalized scattering intensity I_1 in a meridian direction of 5 or less.

The average value of I_2/I_1 is an average value of ratios I_2/I_1 of a normalized scattering intensity I_2 in an equatorial direction to a normalized scattering intensity I_1 in a meridian direction each determined for scattering vectors q in units of 0.000241 in a range of 0.02 nm^{-1} or greater and 0.04 nm^{-1} or less.

The normalized scattering intensity I_2 in the equatorial direction represents voids in the monofilament (micro-cavities in the monofilament). A larger value of the I_2 indicates a greater abundance of voids in the monofilament. Meanwhile, the normalized scattering intensity I_1 in the meridian direction indicates scattering other than that of voids in the monofilament. The average value of the ratio I_2/I_1 being 5 or less indicates that voids in the monofilament are adequately suppressed and that, even when the monofilament is knotted, tensile characteristics similar to those when the monofilament is not knotted are exhibited. The monofilament of the PA4 having an average value of the ratio I_2/I_1 of 5 or less has adequately high tensile characteristics even when knotted.

A lower value of the ratio I_2/I_1 is more preferred from the viewpoint of enhancing tensile characteristics when the monofilament of the PA4 is knotted. For this reason, the ratio I_2/I_1 is more preferably in a range of 1 or greater and 2 or less.

The I_2 and I_1 can be measured by using a known small-angle X-ray scattering measurement device. In addition, the ratio I_2/I_1 can be achieved by a manufacturing method including a first drawing and a second drawing described below, and for example, a smaller drawing ratio in the second drawing tends to result in a smaller I_2 .

Birefringence

[0017] The monofilament of an embodiment of the present invention has a specific birefringence. That is, the birefringence of the monofilament is 50×10^{-3} or greater.

[0018] The birefringence of the monofilament is a scale of degree of orientation with respect to a fiber axial direction of a polymer chain of a polymer compound constituting the monofilament. A larger absolute value of the birefringence indicates a larger degree of orientation. The birefringence of the monofilament being 50×10^{-3} or greater means that the monofilament has been supplied to a drawing process.

[0019] From the viewpoint of enhancing tensile characteristics of the monofilament, the birefringence is preferably 50×10^{-3} or greater, more preferably 55×10^{-3} or greater, and even more preferably 60×10^{-3} or greater. From the viewpoint of exhibiting adequately high tensile characteristics when the monofilament is knotted, the birefringence may be 90×10^{-3} or less.

[0020] The birefringence can be measured by retardation measurement using a polarizing microscope equipped with a Berek compensator and a sodium lamp as a light source. Furthermore, the birefringence tends to be higher when the drawing ratio in the manufacturing method described below is increased.

Tensile Characteristics When Monofilament Is Knotted

[0021] The tensile strength of the monofilament of an embodiment of the present invention when knotted is preferably 550 MPa or greater from the viewpoint of achieving adequate tensile strength for use where the monofilament may be used in a knotted state. An example of use where the monofilament may be used in a knotted state is a fishing line. The tensile strength of the monofilament when knotted can be appropriately selected depending on the use of the monofilament. From the viewpoint of preventing cutting of the monofilament at a knotted position when the monofilament is pulled, the tensile strength of the monofilament when knotted is preferably high and, for example, more preferably 550 MPa or greater, and even more preferably 600 MPa or greater. On the other hand, the tensile strength of the monofilament when knotted may be in a range that can be achieved for the monofilament of the PA4, and from such a viewpoint, the tensile strength of the monofilament when knotted may be 1000 MPa or less.

[0022] The tensile strength of the monofilament when knotted can be measured by using a known instrument that can perform a tensile test for a fiber. The tensile strength of the monofilament when knotted can be achieved by the manufacturing method including the first and the second drawing described below. Furthermore, the tensile strength of the monofilament when knotted tends to be higher when a density of an un-drawn monofilament is lower.

[0023] The elongation at break of the monofilament of an embodiment of the present invention when knotted is preferably 10% or greater from the viewpoint of suppressing breakage when the monofilament is used in a knotted state. The elongation at break of the monofilament when knotted can be appropriately selected depending on the use of the monofilament. From the viewpoint described above, the elongation at break is more preferably 15% or greater, and even more preferably 20% or greater. On the other hand, the elongation at break of the monofilament when knotted may be in a range that can be achieved for the monofilament of the PA4, and from such a viewpoint, the elongation at break of the monofilament when knotted may be 50% or less.

[0024] The elongation at break of the monofilament when knotted can be measured by using a known instrument that can perform a tensile test for a monofilament. The elongation at break of the monofilament when knotted can be achieved by the manufacturing method including the first and the second drawing described below. Furthermore, the elongation at break of the monofilament when knotted tends to be lower when a drawing ratio in the manufacturing method described below is higher, and the elongation at break tends to be higher when a density of an un-drawn monofilament is smaller.

Filament Diameter

[0025] The filament diameter of the monofilament of an embodiment of the present invention is preferably 400 μm or less from the viewpoint of adequately enhancing tensile characteristics when the monofilament is knotted. When the filament diameter is greater than 400 μm , moisture absorption in the second drawing in the manufacturing method described below becomes insufficient, and tensile characteristics when the monofilament is knotted may be insufficient. From the viewpoint of achieving adequate moisture absorption of the monofilament in the second drawing, the filament diameter of the monofilament is more preferably 300 μm or less, and even more preferably 200 μm or less. Meanwhile, the filament diameter of the monofilament may be in a range that can be achieved for the monofilament of the PA4 based on the use of the monofilament; however, from the viewpoint of adequately performing moisture absorption described above, the filament diameter may be 50 μm or greater.

[0026] The filament diameter of the monofilament can be measured by a known technique for measuring a filament diameter, and for example, the measurement can be performed by a known method for measuring the filament diameter of a monofilament by sandwiching the monofilament. The filament diameter of the monofilament tends to be smaller

when the drawing ratio in the manufacturing method described below is higher.

Other Physical Properties

5 **[0027]** The monofilament of an embodiment of the present invention is only required to have the physical properties described above and may further have other physical properties besides those described above, provided that the effect of the present embodiment described above is achieved.

10 **[0028]** For example, the weight average molecular weight of the PA4 in the present embodiment is not limited; however, from the viewpoint of allowing the monofilament to adequately exhibit characteristic physical properties of the PA4, such as mechanical properties and heat resistance, the weight average molecular weight is preferably 20000 or greater, more preferably 30000 or greater, and even more preferably 35000 or greater. The weight average molecular weight of the PA4 is only required to be in a range that can provide the monofilament of the PA4. For example, from such a viewpoint, the weight average molecular weight is preferably 200000 or less, or preferably 100000 or less.

15 Method for Manufacturing Monofilament

[0029] The monofilament of an embodiment of the present invention can be obtained by the manufacturing method described below. The monofilament of an embodiment of the present invention is manufactured by drawing an un-drawn monofilament of polyamide 4 in the first and second drawing described below. By performing such a two-step drawing process, a monofilament of PA4 having excellent tensile characteristics when the monofilament is knotted as described above can be manufactured.

Un-Drawn Monofilament

25 **[0030]** The un-drawn monofilament of polyamide 4 is a monofilament produced by spinning using polyamide 4 as a raw material and, is a monofilament that is substantially not drawn. The un-drawn monofilament is preferably amorphous from the viewpoint of further enhancing tensile characteristics when the monofilament finally manufactured is knotted. From such viewpoints, the density of the un-drawn monofilament is preferably low. From the viewpoint of achieving the above-mentioned tensile characteristics of the monofilament when knotted (tensile strength of the monofilament when knotted is 550 MPa or greater, and elongation at break of the monofilament when knotted is 10% or greater), the density of the un-drawn monofilament is preferably 1.225 g/cm³ or less, and more preferably 1.223 g/cm³ or less.

30 **[0031]** However, even when the density of the un-drawn monofilament is high, the manufacturing method of an embodiment of the present invention can provide a monofilament which has further improved tensile characteristics when knotted. The density of the un-drawn monofilament can be appropriately selected in a range that can exhibit the tensile characteristics when the monofilament is knotted depending on the use of the monofilament, and from such viewpoints, the density may be 1.240 g/cm³ or less, or may be 1.250 g/cm³ or less. Note that the density of the monofilament correlates with the degree of crystallization of the monofilament, and a lower density tends to result in a lower degree of crystallization. For example, the density of the monofilament of 1.230 g/cm³ corresponds to a degree of crystallization of the monofilament of approximately 10%.

40 **[0032]** The density of the un-drawn monofilament can be determined by a method that is also called "density gradient method". The density of the un-drawn monofilament can be adjusted by cooling conditions for the melted and extruded fibrous matter of PA4 obtained by melt spinning. The density of the un-drawn monofilament tends to be lower when a cooling temperature is lower or cooling time is longer.

45 First Drawing

[0033] The first drawing is a process of drawing by dry heat drawing the un-drawn monofilament of polyamide 4 under conditions of a drawing temperature of 40°C or higher and a drawing ratio of 2.5 times or greater and 3.5 times or less. However, when the total drawing ratio described below is 3.5 times, the drawing ratio in the first drawing is less than 3.5 times. The first drawing can be performed by a known technique that can perform drawing in such conditions. When the un-drawn monofilament is drawn to a certain degree under the conditions described above prior to the second drawing, drawing breakage during wet heat drawing can be prevented.

[0034] In the first drawing, the drawing temperature is 40°C or higher. When the drawing temperature in the first drawing is too low, the monofilament may be whitened. From the viewpoint of preventing the whitening of the monofilament, the drawing temperature in the first drawing is preferably 40°C or higher, and more preferably 50°C or higher.

55 **[0035]** When the drawing temperature in the first drawing is high, crystallization of the PA4 of the monofilament may progress and the tensile characteristics when the monofilament is knotted may deteriorate. From the viewpoints of suppressing progression of crystallization and adequately exhibiting tensile characteristics when the monofilament is

knotted, the drawing temperature in the first drawing is preferably 100°C or lower, and more preferably 80°C or lower. The drawing temperature of the first drawing is even more preferably in a range of $60 \pm 5^\circ\text{C}$, and most preferably 60°C from the viewpoint of preventing whitening of the monofilament and exhibiting desired tensile characteristics when the monofilament is knotted.

[0036] In the first drawing, the drawing ratio is 2.5 times or greater and 3.5 times or less. When the drawing ratio in the first drawing is too low, necking remains in a material obtained by subjecting an un-drawn monofilament of PA to the first drawing (primary drawn monofilament) and then local deformation occurs in the second drawing, and the filament diameter of the monofilament may become uneven. From the viewpoint of obtaining a monofilament having a uniform filament diameter, the drawing ratio in the first drawing is preferably 2.5 times or greater, and more preferably 2.8 times or greater.

[0037] When the drawing ratio in the first drawing is too high, the primary drawn monofilament may be drawn excessively, voids may occur, and the desired tensile characteristics when the monofilament is knotted may be insufficient. From the viewpoint of suppressing occurrence of voids in the monofilament, the drawing ratio in the first drawing is preferably 3.5 times or less, and more preferably 3.2 times or less. From the viewpoints of achieving a uniform filament diameter and suppressing occurrence of voids, the drawing ratio in the first drawing is more preferably in a range of 3 ± 0.1 times, and most preferably 3 times.

[0038] The form of drawing in the first drawing is dry heat drawing. The dry heat drawing means drawing of a monofilament in a gas phase (e.g., air) in which the temperature is controlled to the drawing temperature described above. The humidity in the first drawing is not limited and, for example, the relative humidity may be 80% or less.

Second Drawing

[0039] The second drawing is a process of drawing by wet heat drawing the primary drawn monofilament of the polyamide 4 produced in the first drawing under conditions of a drawing temperature of 80°C or higher and 120°C or lower and a drawing ratio of 4 times or greater. The second drawing can be performed by a known technique that can perform drawing in such conditions. By drawing of the primary drawn monofilament in a state where the primary drawn monofilament is allowed to absorb moisture and softened after the first drawing, a monofilament of the PA4 having excellent tensile characteristics when the monofilament is knotted as described above can be manufactured.

[0040] The drawing temperature in the second drawing is 80°C or higher and 120°C or lower. When the drawing temperature in the second drawing is too low, moisture absorption of the primary drawn monofilament tends to be insufficient, and tensile characteristics when the produced monofilament is knotted tends to be insufficient. From the viewpoint of adequate moisture absorption of the primary drawn monofilament, the drawing temperature in the second drawing is preferably 85°C or higher, and more preferably 90°C or higher.

[0041] The drawing temperature of the second drawing can be appropriately set in a range that can achieve a drawing atmosphere by steam. The drawing temperature in the second drawing is preferably 110°C or lower, and more preferably 105°C or lower, from the viewpoint of being able to be set as a drawing atmosphere. From the viewpoints of easily setting up a drawing device and adequate moisture absorption of the primary drawn monofilament, the drawing temperature in the second drawing is even more preferably in a range of $100 \pm 3^\circ\text{C}$, and most preferably 100°C.

[0042] The drawing ratio in the second drawing is 3.5 times or greater. The drawing ratio in the second drawing of an embodiment of the present invention is represented by a final ratio at which the above-mentioned un-drawn monofilament is drawn by both the first and the second drawing (also referred to as "total drawing ratio"). The drawing ratio in the second drawing alone is appropriately selected based on the drawing ratio in the first drawing and the total drawing ratio. The drawing ratio in the second drawing is typically greater than the drawing ratio in the first drawing, and in this case, if the drawing process has only two steps, the total drawing ratio is the same as the drawing ratio in the second drawing.

[0043] When the drawing ratio in the second drawing is too low, tensile characteristics when the monofilament is knotted may deteriorate, and desired tensile characteristics when the monofilament is knotted may not be achieved. From the viewpoint of imparting adequate strength to the monofilament, the drawing ratio in the second drawing is preferably a drawing ratio that makes the total drawing ratio 3.8 times or greater, and more preferably a drawing ratio that makes the total drawing ratio 4 times or greater.

[0044] On the other hand, if a drawing ratio in the second drawing is excessively high, voids may occur in the monofilament. From the viewpoint of adequately suppressing occurrence of voids in the monofilament, the drawing ratio in the second drawing is preferably a drawing ratio that makes the total drawing ratio 5 times or less, and more preferably a drawing ratio that makes the total drawing ratio 4.5 times or less. From the viewpoints of adequately exhibiting tensile characteristics when the monofilament is knotted and adequately suppressing occurrence of voids, the drawing ratio in the second drawing is even more preferably a drawing ratio that makes the total drawing ratio in a range of 4 ± 0.3 times, and most preferably a drawing ratio that makes the total drawing ratio 4 times.

[0045] The form of drawing in the second drawing is wet heat drawing. The wet heat drawing means drawing of a

monofilament in an atmosphere of steam in which the temperature is controlled to the drawing temperature described above. The humidity in the second drawing is not limited and, for example, the relative humidity may be 90% or greater.

[0046] The drawing time in the second drawing is preferably long from the viewpoint of adequately wetting the primary drawn monofilament. From such viewpoints, the drawing time is preferably 5 seconds or longer, more preferably 8 seconds or longer, and even more preferably 10 seconds or longer. On the other hand, the drawing time in the second drawing is preferably short from the viewpoint of productivity of monofilament. From such viewpoints, the drawing time is preferably 60 seconds or shorter, more preferably 45 seconds or shorter, and even more preferably 30 seconds or shorter.

[0047] Furthermore, the filament diameter of the primary drawn monofilament is preferably small from the viewpoint of adequately wetting the primary drawn monofilament in the second drawing. From the viewpoint of achieving the tensile characteristics of the monofilament when knotted (tensile strength of the monofilament when knotted is 550 MPa or greater, and elongation at break of the monofilament when knotted is 10% or greater), the filament diameter of the primary drawn monofilament is preferably 500 μm or less, more preferably 400 μm or less, and even more preferably 300 μm or less.

Other step

[0048] The method for manufacturing the monofilament of an embodiment of the present invention may further include another process besides the first and the second drawing described above, provided that the effects of the embodiment of the present invention can be obtained. For example, the manufacturing method may further include spinning to produce the un-drawn monofilament of the PA4. The form of the spinning is so-called melt spinning, and the spinning may include a melt-extrusion process of extruding a melt-kneaded product of the PA4 by extrusion molding to produce a melted and extruded fibrous matter of the PA4 and a cooling process of cooling the melted and extruded matter produced in the melt-extrusion process in a coolant. Such spinning can be performed by a known melt spinning technique for producing an un-drawn monofilament under liquid cooling.

[0049] In the cooling process, from the viewpoint of decreasing the density of the un-drawn monofilament, the cooling temperature is preferably low and, more specifically, preferably -10°C or lower, more preferably -15°C or lower, and even more preferably -20°C or lower. The cooling temperature can be appropriately selected based on the type of the coolant and manufacturing cost, and in a case where the coolant is a nonpolar solvent described below, from the viewpoint of cost, the cooling temperature may be -60°C or higher.

[0050] In the cooling process, from the viewpoint of decreasing the density of the un-drawn monofilament, the cooling time is preferably long and, more specifically, preferably 0.1 seconds or longer, more preferably 0.2 seconds or longer, and even more preferably 0.3 seconds or longer. From the viewpoint of productivity, the cooling time is preferably short. From such a viewpoint, the cooling time is preferably 5 seconds or shorter, more preferably 3 seconds or shorter, and even more preferably 2 seconds or shorter.

[0051] In the cooling process described above, from the viewpoints of preventing surface roughness of the un-drawn monofilament or preventing occurrence of whitening, the coolant is preferably substantially inert to the melted and extruded matter of the PA4. "Substantially inert" means that substantially no action is applied to the melted and extruded matter, and more specifically indicates being dissolved sparingly or insoluble in PA4 and having no permeability into the melted and extruded matter of the PA4. Such a coolant is preferably a nonpolar solvent. Examples of the nonpolar solvent include silicone oil, hexane, nonane, decane, ethylcyclohexane, isopropylcyclohexane, toluene, and p-cymene.

[0052] Note that, in the spinning, typically, the melted and extruded fibrous matter is cooled while being pulled at a rate greater than a discharging rate of the melted and extruded matter and then supplied to a drawing device. In an embodiment of the present invention, from the melt-extrusion process to the cooling process and the pulling of the melted and extruded matter to supply the melted and extruded matter to the following drawing are not included in the drawing and may be set appropriately in a range in which the effects of the present embodiment can be obtained.

[0053] Furthermore, in the method for manufacturing the monofilament of an embodiment of the present invention, additional drawing that substantially prevents occurrence of voids may be performed after the second drawing. Such additional drawing can be performed by dry heat drawing at a higher temperature compared to other drawing (e.g., 200°C) and appropriate drawing ratio (e.g., 5 times in terms of the final drawing ratio including that of such additional drawing (total drawing ratio)). Such additional drawing is advantageous from the viewpoint of further enhancing tensile characteristics of the monofilament.

Effect

[0054] The method for manufacturing the monofilament of an embodiment of the present invention includes the first and the second drawing described above. The monofilament of the PA4 obtained by the manufacturing method of the present embodiment including these drawings achieves superior tensile characteristics when the monofilament is knotted

compared to a monofilament of PA4 manufactured by drawing other than these drawings. Thus, according to an embodiment of the present invention, occurrence of voids in the monofilament is suppressed and, as a result, a monofilament having improved tensile characteristics when the monofilament is knotted can be provided. More specifically, according to an embodiment of the present invention, a monofilament having high tensile strength and high elongation at break

when the monofilament is knotted can be provided.

[0055] In an embodiment of the present invention, an absorbed moisture quantity of the primary drawn monofilament is reduced by the first drawing, and then wet heat drawing is performed by the second drawing. Consequently, the primary drawn monofilament adequately absorbs moisture and is further drawn in this state, and thus occurrence of voids and crystallization are adequately suppressed. Note that, in dry heat drawing, typically, stress occurred in the monofilament due to drawing tends to be high, and voids tend to be formed. In the voids, stress tends to concentrate when the monofilament is knotted, and from this starting point, the monofilament tends to break. Thus, when the second drawing is performed by dry heat drawing, tensile characteristics when the monofilament is knotted tends to deteriorate.

[0056] Furthermore, in an embodiment of the present invention, even in both the first and the second drawing, drawing is performed at a drawing ratio that is adequately high so that drawing breakage does not occur. Thus, the strength of the monofilament is adequately exhibited. Note that the tensile strength when the monofilament is knotted always becomes smaller than the tensile strength when the monofilament is straight. Thus, when the drawing ratio in the drawing is low, the tensile strength of the obtained monofilament when the monofilament is straight becomes low. Therefore, when the drawing ratio is low, the tensile strength of the obtained monofilament when the monofilament is knotted also becomes low.

[0057] The monofilament of the PA4 obtained by the manufacturing method of the present embodiment can be identified by substantial absence of voids and trace of drawing. The presence and absence of voids can be confirmed by small-angle X-ray scattering method, and the trace of drawing can be confirmed by degree of molecular orientation by the PA4.

[0058] In an embodiment of the present invention, in a case where the filament diameter of the monofilament is adequately small, the filament diameter of the primary drawn monofilament supplied to the second drawing tends to be adequately small based on the drawing ratio in the second drawing, and the primary drawn monofilament may be drawn in a state in which the primary drawn monofilament is adequately wet in the second drawing. For example, the filament diameter of the monofilament of 400 μm or less is advantageous for achieving the tensile characteristics of the monofilament when knotted (tensile strength of the monofilament when knotted is 550 MPa or greater, and elongation at break of the monofilament when knotted is 10% or greater).

[0059] Furthermore, in an embodiment of the present invention, a lower density of the monofilament is advantageous from the viewpoint of enhancing tensile characteristics when the monofilament is knotted. Setting the density of the un-drawn monofilament lower is advantageous from the viewpoint of decrease the density of the monofilament (drawn monofilament). From these viewpoints, the density of the un-drawn monofilament of 1.225 g/cm^3 or less is advantageous from the viewpoint of exhibiting the above-mentioned tensile characteristics when the monofilament is knotted.

[Summary]

[0060] As is clear from the description above, a monofilament according to an embodiment of the present invention is a monofilament of polyamide 4, in a scattering vector in a range of 0.02 nm^{-1} or greater and 0.04 nm^{-1} or less measured by small-angle X-ray scattering, the monofilament having a ratio I_2/I_1 of a normalized scattering intensity I_2 in an equatorial direction to a normalized scattering intensity I_1 in a meridian direction of 5 or less, and an average value of birefringence of the monofilament being 50×10^{-3} or greater.

[0061] Furthermore, a method for manufacturing the monofilament according to an embodiment of the present invention is a method for manufacturing a monofilament of polyamide 4 by drawing an un-drawn monofilament of polyamide 4. The method includes: a first drawing of drawing an un-drawn monofilament of polyamide 4 by dry heat drawing at a drawing temperature of 40°C or higher and a drawing ratio of 2.5 times or greater and 3.5 times or less; and a second drawing of drawing a primary drawn monofilament of the polyamide 4 produced in the first drawing by wet heat drawing at a drawing temperature of 80°C or higher and 120°C or lower and a specific drawing ratio. The specific drawing ratio is a drawing ratio that makes a total drawing ratio 3.5 times or greater, where the total drawing ratio is a final drawing ratio of the un-drawn monofilament caused by both the first and the second drawing. However, when the total drawing ratio is 3.5 times, the drawing ratio in the first drawing is less than 3.5 times.

[0062] According to an embodiment of the present invention, a monofilament of PA4 having high tensile characteristics even when the monofilament is knotted can be thus provided.

[0063] In an embodiment of the present invention, the tensile strength of the monofilament when knotted may be 550 MPa or greater, and the elongation at break of the monofilament when knotted may be 10% or greater. This configuration is even more effective from the viewpoint of providing a monofilament having adequate tensile strength for use where the monofilament may be used in a knotted state.

[0064] In an embodiment of the present invention, the filament diameter of the monofilament may be 400 μm or less.

This configuration is even more effective from the viewpoint of adequately enhancing tensile characteristics when the monofilament is knotted.

[0065] In an embodiment of the present invention, the density of the un-drawn monofilament may be 1.225 g/cm³ or less. This configuration is even more effective from the viewpoint of achieving the tensile characteristics when the monofilament is knotted (tensile strength of the monofilament when knotted is 550 MPa or greater and elongation at break of the monofilament when knotted is 10% or greater).

[0066] The present invention is not limited to each embodiment described above, and may be variously modified within the scope indicated in the claims. Embodiments obtained by appropriately combining technical means disclosed in different embodiments are also included in the technical scope of the present invention.

EXAMPLES

Example 1

[0067] At room temperature, in a polymerization vessel, 2 mol% potassium tert-butoxide was added to α -pyrrolidone and stirred. After potassium tert-butoxide was dissolved, 2 mol% tetramethylammonium chloride as a polymerization auxiliary agent and 0.1 mol% N,N'-adipyl-dipyrrolidone as an initiator were added. After the addition, the system became cloudy and became difficult to be stirred soon. At 72 hours after the stirring was stopped, the aggregate produced in the flask was removed and pulverized. Then, the unreacted product and low-molecular weight substance were washed with acetone. The pulverized product after the washing was then dried, and a powdery PA4 was obtained. The weight average molecular weight (Mw) of the obtained PA4 was 140000.

[0068] The Mw of the PA4 was measured using the following procedure, analysis device and conditions.

Measurement Procedure

[0069] In hexafluoroisopropanol (HFIP) in which sodium trifluoroacetate was dissolved at a concentration of 5 mM, 10 mg of the PA4 sample obtained as described above was dissolved to prepare a solution of 10 cm³, and then the solution was filtered using a membrane filter to obtain a sample solution. An amount of 10 μ L of the sample solution was injected into the analysis device described below, and the weight average molecular weight of the PA4 was measured under the measurement conditions described below. Note that, in the present specification, the wording "from A to B" represents a range including numerical values on both ends, which is a range of A or greater and B or less.

[Analyzer]

GPC apparatus: HLC-8420 GPC, available from TOSOH CORPORATION

[Measurement conditions]

[0070]

A) Column: GPC HFIP806M $\times$ 2 (connected in series), available from Shoko Science Co., Ltd.

B) Eluent: 5 mM CF₃COONa/HFIP

C) MALS: DAWN HELEOS 2, available from Wyatt Technology Co.

D) 10 to 11 mg of sample/5 mM CF₃COONa/10 mL of HFIP

E) Flow rate: 1.0 mL/min

F) dn/dc: 0.240

[0071] The PA4 was molded in a fibrous form by melt-extrusion at a temperature of 265°C, and immediately after the molding, the obtained melted and extruded fibrous matter was passed through a volatile silicone oil ("KF-995", available from Shin-Etsu Chemical Co., Ltd.) bath at -20°C for 0.3 seconds, and cooled and solidified. An un-drawn monofilament of the PA4 was thus produced. The density of the un-drawn monofilament was determined by the following method, and the density of the un-drawn monofilament was 1.220 g/cm³.

Measurement Method of Density

[0072] The density of the un-drawn monofilament was determined by a density gradient method. As the solvent, 6 types of mixed solvents, in which the densities were adjusted to a range of 1.20 to 1.30 g/cm³ and varied in 0.02 increments by changing the mixing ratio of heptane and carbon tetrachloride, were used.

[0073] Then, the produced un-drawn monofilament was drawn by dry heat drawing at a drawing temperature of 60°C and a drawing ratio of 3.0 times. A humidity of an atmosphere during dry heat drawing was 10%RH or less. Then, as the second stage drawing (secondary drawing), the produced primary drawn monofilament was drawn by wet heat drawing at a drawing temperature of 100°C and a total drawing ratio of 4.0 times. A humidity of an atmosphere during

wet heat drawing was 100%RH or less. Thus, the monofilament of the drawn monofilament of the PA4 was produced.
[0074] The filament diameter of the produced monofilament was measured by sandwiching the monofilament by a micrometer. For each of five randomly chosen monofilaments, the filament diameter was measured at one freely selected point in a length direction thereof, and an average value of the obtained measured values was determined and used as the filament diameter of the monofilament. The filament diameter of the monofilament was 168 μm .

Example 2

[0075] A monofilament was produced in the same manner as in Example 1 except for changing the drawing ratio of the primary drawn monofilament in the wet heat drawing of the secondary drawing to 4.8 times in terms of the total drawing ratio. The filament diameter of the monofilament was 147 μm .

Example 3

[0076] A monofilament was produced in the same manner as in Example 1 except for changing the temperature of the silicone oil bath for cooling the melted and extruded fibrous matter to 40°C. The density of the un-drawn monofilament was 1.239 g/cm³.

Example 4

[0077] A monofilament was produced in the same manner as in Example 1 except for changing the primary drawing ratio of the un-drawn monofilament to 2.5 times.

Example 5

[0078] A monofilament was produced in the same manner as in Example 1 except for changing the primary drawing ratio of the un-drawn monofilament to 3.5 times.

Example 6

[0079] A monofilament was produced in the same manner as in Example 1 except for changing the primary drawing temperature of the un-drawn monofilament to 50°C.

Example 7

[0080] A monofilament was produced in the same manner as in Example 1 except for changing the primary drawing temperature of the un-drawn monofilament to 100°C.

Comparative Example 1

[0081] A monofilament was produced in the same manner as in Example 1 except for changing the drawing temperature (secondary drawing temperature) in the secondary drawing of the primary drawn monofilament to 200°C and drawing the primary drawn monofilament by dry heat drawing in place of wet heat drawing.

Comparative Example 2

[0082] A monofilament was produced in the same manner as in Example 3 except for changing the secondary drawing temperature to 200°C and subjecting the primary drawn monofilament to the secondary drawing by dry heat drawing in place of wet heat drawing.

Comparative Example 3

[0083] A monofilament was produced in the same manner as in Example 3 except for changing the secondary drawing temperature to 200°C, changing the drawing ratio to 4.6 times in terms of the total drawing ratio, and subjecting the

primary drawn monofilament to the secondary drawing by dry heat drawing in place of wet heat drawing.

Comparative Example 4

5 **[0084]** It was attempted to produce a monofilament in the same manner as in Example 3 except for changing the secondary drawing temperature to 200°C, changing the drawing ratio to 4.8 times in terms of the total drawing ratio, and subjecting the primary drawn monofilament to the secondary drawing by dry heat drawing in place of wet heat drawing. Drawing breakage occurred in the secondary drawing, and drawing could not be performed.

10 Comparative Example 5

[0085] It was attempted to produce a monofilament of a PA4 by drawing an un-drawn monofilament by wet heat drawing at a drawing temperature of 100°C and a drawing ratio of 3.0 times. Drawing breakage occurred in the wet heat drawing, and drawing could not be performed.

15 Comparative Example 6

[0086] A monofilament was produced in the same manner as in Comparative Example 1 except for changing the primary drawing ratio of the un-drawn monofilament to 2.5 times.

20 Comparative Example 7

[0087] A monofilament was produced in the same manner as in Comparative Example 1 except for changing the primary drawing ratio of the un-drawn monofilament to 3.5 times.

25 Comparative Example 8

[0088] A monofilament was produced in the same manner as in Comparative Example 1 except for changing the primary drawing temperature of the un-drawn monofilament to 50°C.

30 Comparative Example 9

[0089] A monofilament was produced in the same manner as in Comparative Example 1 except for changing the primary drawing temperature of the un-drawn monofilament to 100°C.

35 Comparative Example 10

[0090] A monofilament was produced in the same manner as in Comparative Example 1 except for performing no secondary drawing.

40 Evaluation

Scattering Vector Determined by Small-Angle X-Ray Scattering (SAXS)

45 **[0091]** For each of the monofilaments in Examples and Comparative Examples above, a normalized scattering intensity I1 in a meridian direction and a normalized scattering intensity I2 in an equatorial direction were measured by the measurement methods described below, and a ratio I2/I1 was determined. The ratio I2/I1 is an average value of all ratios I2/I1 determined for scattering vectors q in a range of 0.02 nm⁻¹ or greater and 0.04 nm⁻¹ or less in units of 0.000241.

50 Measurement Method of Normalized Scattering Intensity

[0092] A fiber sample obtained by bundling 16 monofilaments was placed in a cell, and X-ray scattering measurement was performed in a state where the fiber sample was immersed in tetradecane in the following conditions.

55 Instrument: Nano-Viewer, available from Rigaku Corporation X-ray source: CuK α
Current-voltage: 40 kV - 20 mA
Irradiation time: 45 min
Camera length: 830 mm (small angle)

Slit: 0.7 mmΦ - 0.6 mmΦ - 0.8 mmΦ

Birefringence of Monofilament

- 5 **[0093]** For each of the monofilaments in Examples and Comparative Examples above, a birefringence of a monofilament was measured by the measurement methods described below.

Measurement Method of Birefringence

- 10 **[0094]** The birefringence of the monofilament was determined by retardation measurement using a polarizing microscope equipped with a Berek compensator and a sodium lamp as a light source.

Tensile Characteristics of Monofilament When Knotted

- 15 **[0095]** For each of the monofilaments in Examples and Comparative Examples above, a tensile strength and an elongation at break of the monofilament when knotted were measured by the measurement methods described below. A case where the tensile strength of the monofilament when knotted was 550 MPa or greater and the elongation at break of the monofilament when knotted was 10% or greater was considered to have no problem for practical use even when the monofilament is used by being knotted, like a fishing line.

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Measurement Method of Tensile Strength and Elongation at Break

- 25 **[0096]** By using Tensilon RTF-1210 as a tester, tensile measurement was performed by setting a distance between chucks to 150 mm and a tensile test speed to 150 mm/min at 23°C and a humidity of 50%RH. When the monofilament was knotted, the knotted part was placed at a center of the chucks.

- 30 **[0097]** The production conditions and properties of the monofilaments in Examples and Comparative Examples described above are shown in Table 1. Furthermore, FIG. 1 is a photograph of two-dimensional image of the monofilament of Example 1 by SAXS. FIG. 2 is a photograph of two-dimensional image of the monofilament of Comparative Example 1 by SAXS. In FIGS. 1 and 2, an arrow I1 indicates a meridian direction in the two-dimensional image by SAXS, and an arrow I2 indicates an equatorial direction in the two-dimensional image by SAXS.

[Table 1]

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[0098]

Table 1

	Drawing conditions					Monofilament				
	Un-drawn monofilament density [g/cm ³]	Drawing temperature [°C]		Stretching ratio [-]		I2/I1 [-]	Birefringence [×10 ⁻³]	Tensile characteristics when knotted		Filament diameter [μm]
		First	Second	First	Total			Tensile strength (MPa)	Elongation at break [%]	
Example 1	1.220	60	Wetheat 100	3.0	4.0	1.5	58.5	604	28	168
Example 2	1.220	60	Wetheat 100	3.0	4.8	2.8	64.4	607	13	154
Example 3	1.239	60	Wetheat 100	3.0	4.0	1.9	60.2	562	19	168
Example 4	1.220	60	Wetheat 100	2.5	4.0	1.1	58.1	570	28	168
Example 5	1.220	60	Wetheat 100	3.5	4.0	14	58.3	620	29	168
Example 6	1.220	50	Wetheat 100	3.0	4.0	2.1	59.2	572	30	168
Example 7	1.220	100	Wetheat 100	3.0	4.0	1.8	60.4	565	33	168
Comparative Example 1	1.220	60	200	3.0	4.0	10.2	64.5	471	15	168
Comparative Example 2	1.239	60	200	3.0	4.0	14.4	64.8	456	10	168
Comparative Example 3	1.239	60	200	3.0	4.6	65.4	66.8	357	7	157
Comparative Example 4	1.239	60	200	3.0	4.8	-	-	Drawing was not possible		-
Comparative Example 5	1.239	Wetheat 100	-	3.0	-	-	-	Drawing was not possible		-

(continued)

	Drawing conditions					Monofilament				
	Un-drawn monofilament density [g/cm ³]	Drawing temperature [°C]		Stretching ratio [-]		I2/I1 [-]	Birefringence [×10 ⁻³]	Tensile characteristics when knotted		Filament diameter [μm]
		First	Second	First	Total			Tensile strength (MPa)	Elongation at break [%]	
Comparative Example 6	1.220	60	200	2.5	4.0	9.3	63.5	455	17	168
Comparative Example 7	1.220	60	200	3.5	4.0	10.3	64.7	464	16	168
Comparative Example 8	1.220	50	200	3.0	4.0	9.8	64.2	452	15	168
Comparative Example 9	1.220	100	200	3.0	4.0	11.2	63.2	432	14	168
Comparative Example 10	1.220	60	-	3.0	-	1.3	36.2	471	69	193

Discussion of Examples and Comparative Examples

[0099] As is clear from FIG. 1, the monofilament of Example had a small void scattering (scattering originated from voids) in a center in the equatorial direction in the two-dimensional image by SAXS. Furthermore, as is clear from Table 1, I₂/I₁ of each of the monofilaments of Examples was 5 or less, and the birefringence was 50×10^{-3} or greater. The monofilament of each of Examples had improved tensile characteristics when the monofilament was knotted compared to those of the monofilaments of Comparative Examples. Furthermore, each of Examples 1, 2, and 4 to 7, in which density of the un-drawn monofilament was even lower, had a higher tensile strength when the monofilament was knotted compared to that of Example 3.

[0100] On the other hand, in each of Comparative Examples 1 to 3 and 7 to 9, tensile characteristics when the monofilament was knotted substantially deteriorated compared to those of Examples. Furthermore, as is clear from FIG. 2, in the monofilament of Comparative Example 1, an intense streak was observed in a center in the equatorial direction in the two-dimensional image of SAXS, and thus void scattering was observed. It is conceived that this is because voids were formed in an inner part of the monofilament due to performance of the second drawing at a high drawing temperature and a high drawing ratio.

[0101] Furthermore, in Comparative Example 4, drawing breakage occurred in the drawing of the primary drawn monofilament. In Comparative Example 5, drawing breakage occurred in the drawing of the un-drawn monofilament. It is conceived that, in Comparative Example 4, this is because voids occurred because the un-drawn monofilament was drawn without wetting, and thus breakage occurred. In Comparative Example 5, it is conceived that the effect of reduction in strength due to wetting of the un-drawn monofilament was greater than the effect of improvement in the strength due to drawing of the un-drawn monofilament.

[0102] As is clear from the comparison of Comparative Example 1 and Comparative Example 10 and Examples, for the monofilament of each of Examples, the tensile strength tends to be even higher by the wet heat secondary drawing among tensile characteristics exhibited by the dry heat drawing of the un-drawn monofilament. Furthermore, regarding elongation at break, the secondary drawing by wet heat drawing tends to cause less reduction in elongation at break due to the secondary drawing compared to the secondary drawing by dry heat drawing. Furthermore, according to Examples 1 to 7, the balance between the tensile strength and the elongation at break is expected to be adequately adjusted by adjusting the conditions of the dry heat primary drawing and the wet heat secondary drawing.

[0103] Note that it is conceived that, since the PA4 has a relatively high hydrophilicity, the strength of the monofilament decreases in the presence of water. Thus, it is conceived that dry heat drawing is advantageous for exhibition of the strength of the monofilament of the PA4. Thus, it is conceived that, in a case of a polyamide having a hydrophobicity that is higher than the hydrophobicity of the PA4, e.g., PA6, effect of moisture absorption during drawing is smaller. Therefore, it is conceived that, in a case of an un-drawn monofilament of PA6, the strength is adequately improved even when the drawing is performed by wet heat drawing.

INDUSTRIAL APPLICABILITY

[0104] The monofilament of the PA4 of an embodiment of the present invention can be used as a synthetic fiber having excellent tensile characteristics. According to an embodiment of the present invention, environmental damage upon use of the synthetic fiber is expected to be further reduced.

Claims

1. A monofilament of polyamide 4,
in a scattering vector in a range of 0.02 nm^{-1} or greater and 0.04 nm^{-1} or less measured by small-angle X-ray scattering, the monofilament having an average value of a ratio I₂/I₁ of a normalized scattering intensity I₂ in an equatorial direction to a normalized scattering intensity I₁ in a meridian direction of 5 or less, and a birefringence of the monofilament being 50×10^{-3} or greater.
2. The monofilament according to claim 1, wherein a tensile strength of the monofilament when knotted is 550 MPa or greater, and an elongation at break of the monofilament when knotted is 10% or greater.
3. The monofilament according to claim 1 or 2, wherein a filament diameter is 400 μm or less.
4. A method for manufacturing a monofilament of polyamide 4 by drawing an un-drawn monofilament of polyamide 4, the method comprising:

EP 4 353 880 A1

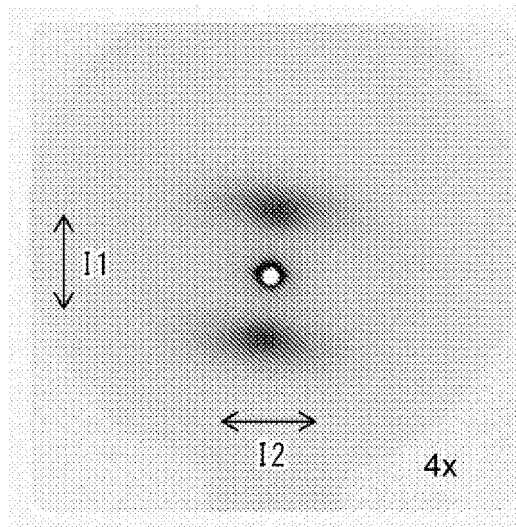
a first drawing of drawing an un-drawn monofilament of polyamide 4 by dry heat drawing at a drawing temperature of 40°C or higher and a drawing ratio of 2.5 times or greater and 3.5 times or less; and

a second drawing of drawing a primary drawn monofilament of the polyamide 4 produced in the first drawing by wet heat drawing at a drawing temperature of 80°C or higher and 120°C or lower and a specific drawing ratio; the specific drawing ratio being a drawing ratio that makes a total drawing ratio 3.5 times or greater, the total drawing ratio being a drawing ratio of the un-drawn monofilament caused by both the first and the second drawing, and

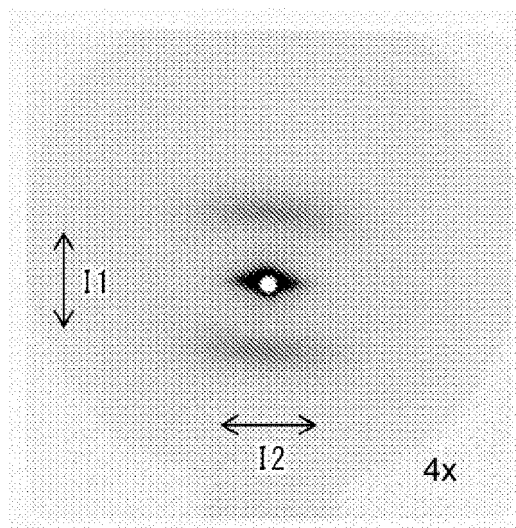
when the total drawing ratio is 3.5 times, the drawing ratio in the first drawing being less than 3.5 times.

- 5.** The method for manufacturing a monofilament according to claim 4, wherein a density of the un-drawn monofilament is 1.225 g/cm³ or less.

[FIG. 1]



[FIG. 2]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/020954

A. CLASSIFICATION OF SUBJECT MATTER <i>D01F 6/60</i> (2006.01)i FI: D01F6/60 341B; D01F6/60 301C; D01F6/60 311K 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) D01F6/60; C08G69/00-69/50 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2022 Registered utility model specifications of Japan 1996-2022 Published registered utility model applications of Japan 1994-2022 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)															
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>JP 2019-137934 A (BRIDGESTONE CORP) 22 August 2019 (2019-08-22) example 1</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>JP 2021-31790 A (BRIDGESTONE CORP) 01 March 2021 (2021-03-01) example 1</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>JP 55-6726 B2 (MITSUBISHI CHEM IND LTD.) 19 February 1980 (1980-02-19) examples</td> <td>1-5</td> </tr> <tr> <td>A</td> <td>JP 4-136215 A (KURARAY CO LTD) 11 May 1992 (1992-05-11) examples 1-3</td> <td>1-5</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	JP 2019-137934 A (BRIDGESTONE CORP) 22 August 2019 (2019-08-22) example 1	1-5	A	JP 2021-31790 A (BRIDGESTONE CORP) 01 March 2021 (2021-03-01) example 1	1-5	A	JP 55-6726 B2 (MITSUBISHI CHEM IND LTD.) 19 February 1980 (1980-02-19) examples	1-5	A	JP 4-136215 A (KURARAY CO LTD) 11 May 1992 (1992-05-11) examples 1-3	1-5
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A	JP 4-136215 A (KURARAY CO LTD) 11 May 1992 (1992-05-11) examples 1-3	1-5													
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.															
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Date of the actual completion of the international search 08 June 2022	Date of mailing of the international search report 21 June 2022														
Name and mailing address of the ISA/JP Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan	Authorized officer Telephone No.														

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/020954

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REFERENCES CITED IN THE DESCRIPTION

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