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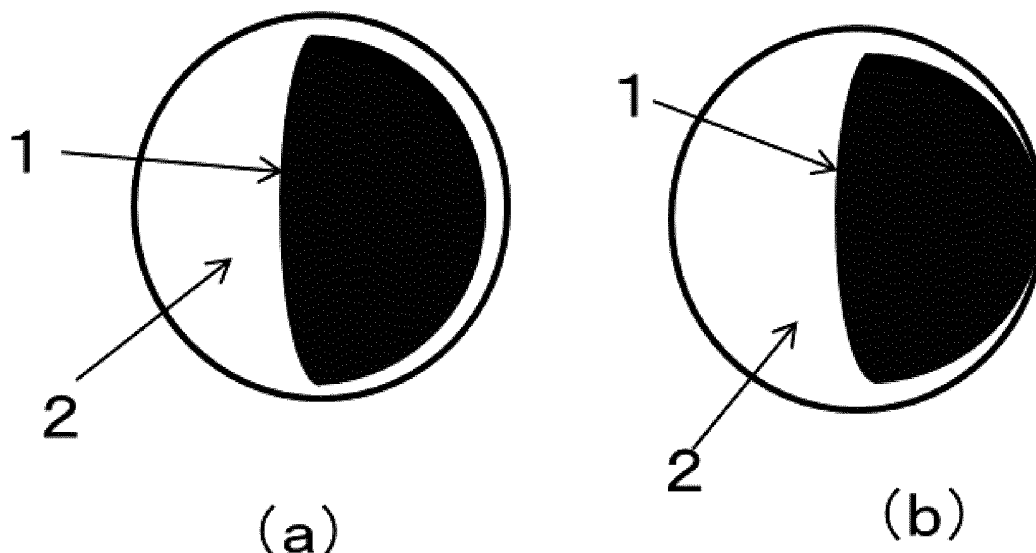
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(54) **POLYURETHANE-NYLON 6 ECCENTRIC SHEATH-CORE CONJUGATE FIBER**

(57) The purpose of the present invention is to provide a polyurethane-nylon 6 eccentric sheath-core conjugate fiber which can obtain an excellent soft stretchable woven/knitted fabric and ensure the appearance quality of stockings. The present invention relates to an eccentric

sheath-core conjugate fiber being characterized by having: (1) a core component of a thermoplastic polyurethane; and (2) a sheath component of nylon 6, wherein the curvature of a cross section is 15% or less and the CV value of the curvature of a cross section is 0.40 or less.

[Fig. 1]



Description

TECHNICAL FIELD

[0001] The present invention relates to an eccentric sheath-core conjugate fiber containing polyurethane and nylon 6.

BACKGROUND ART

[0002] A self-crimped conjugate fiber obtained by eccentrically conjugating a polyurethane and a polyamide can be made into a knitted fabric having excellent crimp properties and having a soft stretchability and transparency, and is therefore highly rated as a high-grade stocking material.

[0003] On the other hand, in stockings using the self-crimped conjugate fiber, there is a problem that variations in the crimp properties of the fiber tends to directly cause a knitted fabric defect such as streaks or unevenness. In order to avoid the knitted fabric defect such as streaks or unevenness, all self-crimped conjugate fibers are subjected to a crimp property inspection and a knitting inspection, and are selected for use. Therefore, there is a demand for the self-crimped conjugate fiber in which variations in the crimp properties of the fiber are small, and the streak, unevenness, and the like hardly occur when made into stockings.

[0004] In the related art, many studies have been made on the self-crimped conjugate fiber obtained by eccentrically conjugating polyurethane and polyamide. For example, Patent Literature 1 describes a self-crimped conjugate fiber, which comprises a polyurethane composition containing at least 10% by weight of a polycarbonic acid ester-based polyurethane as a copolymerization component or a mixing component, and having a dimethylacetamide relative viscosity of from 1.80 to 3.00, improves stability during conjugate spinning and filature, and reduces variations between polymers of a polyurethane elastomer.

[0005] Patent Literature 2 discloses a self-crimped conjugate filament obtained by conjugated melt spinning of polyamide and polyurethane elastomer, which is obtained by adding and mixing 5% to 20% by weight of a polyisocyanate compound having a molecular weight of 400 or more to a thermoplastic polyurethane in a molten state, at a conjugating weight ratio of 80/20 to 20/80 as if being eccentrically disposed and conjugated in a cross-section of a single filament, followed by stretching and subsequent relaxation heat treatment. The filament has a dissolution reduction ratio of the polyurethane elastomer to dimethylformamide of 80% by weight or less, a linear shrinkage ratio of the filament of about 10%, and the crimp expression ratio of 68% or more. The filament has excellent peel resistance between polyamide and a polyurethane elastomer, and sufficient crimp expression strength and stretch-recovery properties of the crimp even after relaxation heat treatment.

CITATION LIST

PATENT LITERATURE

[0006]

Patent Literature 1: JP-A-2-80616

Patent Literature 2: JP-B-7-91693

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0007] However, although the conjugate fiber described in Patent Literature 1 is excellent in melt spinning stability and filature properties and enables to industrially produce a conjugate fiber having stable physical properties, there is no suggestion about variations in crimp properties. There remains a problem in that the crimp variations tend to directly cause a knitted fabric defect such as a streak or unevenness.

[0008] The conjugate fiber described in Patent Literature 2 is excellent in peeling resistance of the polyamide and polyurethane elastomer, and has the crimp expression strength and the stretch-recovery properties of the crimp, but there is no suggestion about variations in the crimp properties. There remains a problem in that the crimp variations tend to directly cause a knitted fabric defect such as a streak or unevenness.

[0009] Thus, an object of the present invention is to provide a polyurethane-nylon 6 eccentric sheath-core conjugate fiber which can overcome the problems in the related art and provide an excellent soft stretchable woven/knitted fabric and appearance quality of stockings.

SOLUTION TO PROBLEM

[0010] To solve the above problem, the present invention has the following constitution.

- (1) An eccentric sheath-core conjugate fiber including a core component, which is thermoplastic polyurethane, and a sheath component, which is nylon 6, in which the eccentric sheath-core conjugate fiber has cross-sectional curvature of 15% or less and a cross-sectional curvature CV value of 0.40 or less.
- (2) The eccentric sheath-core conjugate fiber according to (1), having a stretch and elongation rate of 90% or more.
- (3) A woven/knitted fabric comprising the eccentric sheath-core conjugate fiber according to (1) or (2) in at least a part thereof.
- (4) Stockings comprising the eccentric sheath-core conjugate fiber according to (1) or (2) in at least a part of a leg portion thereof.

ADVANTAGEOUS EFFECTS OF INVENTION

[0011] According to the present invention, it is possible to provide a polyurethane-nylon 6 eccentric sheath-core conjugate fiber by which an excellent soft stretchable woven/knitted fabric and appearance quality of stocking can be obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0012]

Fig. 1(a) and Fig. 1(b) are model diagrams illustrating an example of a cross section of an eccentric sheath-core conjugate fiber of the present invention.

Fig. 2 is a model diagram of measurement of a cross-sectional curvature of the eccentric sheath-core conjugate fiber of the present invention.

DESCRIPTION OF EMBODIMENTS

[0013] The eccentric sheath-core conjugate fiber of the present invention is a latent crimpable yarn which is expressed as a coiled crimp in a production process of a woven/knitted fabric and stockings (hereinafter, referred to as a high-level process). In particular, since knitted fabrics such as stockings is knitted by supplying a plurality of yarns to a knitting machine, when yarns having different latent crimpabilities are supplied and knitted, even if a defect such as a streak or non-uniformity is not found immediately after knitting, crimp variations occur in the high-level process, resulting in the defect such as a streak or unevenness.

[0014] The present inventors have found that by controlling an interface on a cross section of the eccentric sheath-core fiber before expression of the crimp, a stable crimp can be expressed, crimp variations are prevented, and a soft stretchable woven/knitted fabric or stockings excellent in appearance quality without a streak or unevenness is obtained.

[0015] The eccentric sheath-core conjugate fiber of the present invention includes a core component composed of thermoplastic polyurethane and a sheath component composed of nylon 6.

[0016] In the present invention, the "eccentric sheath-core" indicates that the position of the center of gravity of the thermoplastic polyurethane of a core portion is different from the center of the cross section of the conjugate fiber in the cross section of the conjugate fiber. Specifically, modes as shown in Fig. 1(a) and Fig. 1(b) are referred to. The eccentric sheath-core structure enables to express a uniform coiled crimp. Further, due to a difference in viscosity between the core component thermoplastic polyurethane and the sheath component nylon 6, the thermoplastic polyurethane at the interface therebetween is slightly convex and curved. Although the core component may be partially exposed as shown in Fig. 1(b), it is more preferable that the sheath component nylon 6 contains a thermoplastic polyurethane which is a core component as shown in Fig. 1(a).

[0017] A minimum thickness of the nylon 6 of the sheath component covering the core component is preferably 0.01 to 0.1 times of a diameter of the conjugate fiber, more preferably 0.02 to 0.08 times. In this range, sufficient ability for crimp expression and a stretch performance can be obtained. A conjugate ratio of the eccentric sheath-core conjugate fiber is preferably 80/20 to 20/80. When a ratio of the polyurethane becomes higher than the conjugate ratio of 80/20 and the nylon ratio becomes smaller than the conjugate ratio of 80/20, dyeability and durability deteriorate, and usefulness is poor. When the polyurethane ratio is smaller than the conjugate ratio of 20/80 and the nylon ratio is larger than the conjugate ratio of 20/80, expression of the crimp is insufficient. From the viewpoint of expression of uniform coiled crimps and excellent soft stretchability, it is more preferably 40/60 to 60/40.

[0018] The eccentric sheath-core conjugate fiber of the present invention needs to have a cross-sectional curvature of 15% or less. The cross-sectional curvature herein indicates a degree of curvature of the interface between the core

component thermoplastic polyurethane and the sheath component nylon 6, the larger a numerical value is, the larger the degree of curvature of the interface is, and smaller crimps are expressed; the smaller the numerical value is, the smaller the degree of curvature of the interface is, and larger crimps are expressed.

[0019] By setting the cross-sectional curvature to 15% or less, uniform and dense crimps are expressed, and the soft stretchable woven/knitted fabric and stockings, which provide an excellent soft stretchability or appearance quality, can be obtained. The cross-sectional curvature is preferably 0 to 10%. It is more preferably 0 to 5%.

[0020] The eccentric sheath-core conjugate fiber of the present invention needs to have a cross-sectional curvature CV value of 0.40 or less. In particular, in the stockings, since a sock knitting machine of 4-port yarn feeding is a mainstream, it is necessary to evaluate for four yarns constituting the stockings. Therefore, the cross-sectional curvature CV value is a value obtained by measuring a cross section of all filaments of the four eccentric sheath-core conjugate fibers and dividing a standard deviation thereof by an average value thereof. By setting the CV value in such a range, the soft stretchable woven/knitted fabric and stockings having less crimp variations and excellent appearance quality without a streak or unevenness can be obtained. The range is more preferably 0.20 or less.

[0021] The eccentric sheath-core conjugate fiber of the present invention preferably has a stretch and elongation rate of 90% or more. By setting the stretch and elongation rate in such a range, uniform and dense coil crimps are expressed, and the soft stretchable woven/knitted fabric and stockings, which provide excellent soft stretchability or appearance quality, can be obtained. The range is more preferably 100% or more.

[0022] The eccentric sheath-core conjugate fiber of the present invention preferably has a strength of 2.5 cN/dtex or more from the viewpoint of productivity in the high-level process and durability of clothing. The strength is more preferably 3.0 cN/dtex or more.

[0023] Elongation of the eccentric sheath-core conjugate fiber of the present invention is preferably 35% or more from the viewpoint of productivity in the high-level process. The elongation is more preferably 40% to 65%.

[0024] The total fineness or the number of filaments of the eccentric sheath-core conjugate fiber of the present invention can be arbitrarily designed in terms of stretchability or texture required for clothing use. Considering the clothing use, the total fineness of 5 dtex to 235 dtex and the number of filaments of 1 to 144 are preferable. For example, in stockings use, the total fineness of 5 dtex to 33 dtex and the number of filaments of 1 to 3 are preferable.

[0025] In the eccentric sheath-core conjugate fiber of the present invention, to control the cross-sectional curvature and the cross-sectional curvature CV value in such a range, in addition to polymer selection of thermoplastic polyurethane and nylon 6, and an antioxidant, melting conditions (polymer temperature, polymer temperature difference, spinning temperature, and the like) in a previous stage of forming the eccentric sheath-core conjugate cross section are combined to more preferably control.

[0026] The thermoplastic polyurethane used in the present invention is a polymer compound obtained by a reaction of three components of a diisocyanate, a polyol, and a chain extender.

[0027] Specific examples of the diisocyanate include trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, 1,3-bis(isocyanato methyl) cyclohexane, 1,4-bis(isocyanato methyl) cyclohexane, 1,3-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, 2,2'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, and diphenylmethane diisocyanate. In view of reactivity, diphenylmethane diisocyanate is preferred.

[0028] Specific examples of the polyol include, but are not limited to, polyether polyol, polyester polyol, polycaprolactone polyol, and polycarbonate polyol, and the polyol may be used alone or in combination of two or more thereof. In view of heat resistance, the polycarbonate polyol is preferred.

[0029] Specific examples of the chain extender include ethane diol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, and dipropylene glycol. In view of reactivity, 1,4-butanediol is preferred.

[0030] Weight average molecular weight (Mw) of the thermoplastic polyurethane used in the core portion in the eccentric sheath-core conjugate fiber of the present invention is preferably 80,000 or more and 180,000 or less. By setting the Mw to 80,000 or more, thermal degradation within a preferable polymer temperature range, which is described later, can be prevented, and filature properties becomes good. By setting the Mw to 180,000 or less, a difference in melt viscosity from nylon 6 can be reduced, and the cross-sectional curvature can be set to 15% or less. The Mw is more preferably 80,000 or more and 140,000 or less.

[0031] A relationship M_z/M_w between an average molecular weight (M_z) and the weight average molecular weight (M_w) of the thermoplastic polyurethane is preferably 3.0 or less. The M_z/M_w is an index indicating spread to a high side, and by setting the M_z/M_w to this range, variations in melt viscosity decrease, so that the cross-sectional curvature CV value can be set to 0.40 or less.

[0032] Further, since the thermoplastic polyurethane is a polymer which easily undergoes thermal degradation, thermal decomposition easily occurs within the preferred polymer temperature range, which is described later, and the filature properties are affected. In addition, the thermal decomposition causes a decrease in the molecular weight, leading to increase in difference in melt viscosity from nylon, and hence not only the curvature ratio increases, but also a melt

viscosity spot occurs, leading to deterioration of the cross-sectional curvature. Therefore, it is preferable to add a hindered phenol-based stabilizer, which is a radical-supplementing antioxidant, to the thermoplastic polyurethane of the core portion.

[0033] An amount of the hindered phenol-based stabilizer is preferably 0.1% by weight or more and 1.0% by weight or less with respect to the weight of thermoplastic polyurethane. By setting the amount to 0.1% by weight or more, thermal degradation of the thermoplastic polyurethane polymer within the preferred polymer temperature range, which is described later, can be prevented, and variations in viscosity or yarn breakage can be prevented. By setting the amount to 1.0% by weight or less, no precipitation of the antioxidant occurs on a fiber surface and thus it is preferred. Another antioxidant such as HALS, a phosphorus-based one, or a sulfur-based one may be used in combination as necessary.

[0034] Examples of the hindered phenol-based stabilizer include pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] (IR 1010), 2,4,6-tris (3',5'-di-tert-butyl-4-hydroxybenzyl) mesitylene (IR 1330), (1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxyphenyl) benzene (AO-330), 1,3,5-tris [[3,5-bis (1,1-dimethylethyl)-4-hydroxyphenyl] methyl]-1,3,5-triazine-2,4,6 (1H, 3H, 5H)-trione (IR3114), and N,N'-hexamethylene bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanamide] (IR1098).

[0035] Various additives such as a delustering agent, a flame retardant, an ultraviolet ray absorber, an infrared ray absorber, a crystal nucleating agent, a fluorescent brightening agent, an antistatic agent, a hygroscopic polymer, and carbon may be added to the thermoplastic polyurethane of the core portion in the present invention. In the case of addition, copolymerization or mixing may be performed as necessary in a total additive content of 0.001% to 10% by weight.

[0036] Various additives such as a delustering agent, a flame retardant, an antioxidant, an ultraviolet ray absorbent, an infrared ray absorbent, a crystal nucleating agent, a fluorescent brightening agent, an antistatic agent, a hygroscopic polymer, and carbon may be added to nylon 6 of the sheath portion of the present invention. In the case of addition, copolymerization or mixing may be performed as necessary in a total additive content of 0.001% to 10% by weight.

[0037] Sulfuric acid relative viscosity of the sheath portion nylon 6 of the present invention is preferably 2.0 or more and 2.3 or less. By setting the sulfuric acid relative viscosity in such a range, a difference in melt viscosity from the thermoplastic polyurethane can be reduced, cross-sectional formability can be stabilized, and the cross-sectional curvature can be set to 15% or less.

[0038] The eccentric sheath-core conjugate fiber of the present invention can be produced by publicly known melt spinning and conjugate spinning methods. For example, the thermoplastic polyurethane (core portion) and the nylon 6 (sheath portion) are separately melted, supplied to a spinning pack, and discharged from a conjugate spinning spinneret for an eccentric sheath-core type to form yarn. A method of forming the eccentric sheath-core structure is not particularly limited, and for example, there is a method in which a thin sheath of nylon 6 concentrically covers on a polyurethane and a flow of second nylon 6 is conjugated therewith side by side, or a method in which the polyurethane and nylon 6 are conjugated in a side-by-side form, and then a thin sheath of nylon 6 covers thereon. The yarn is uniformly cooled to room temperature by a cooling device provided in a downstream side of the conjugate spinning spinneret, and then an oil agent is applied and the yarn is wound at a low speed. Thereafter, the yarn is preferably stretched by 3 to 5 times.

[0039] The melt viscosity at 210°C of the thermoplastic polyurethane is preferably 5,000 poise to 18,000 poise. By setting the melt viscosity in such a range, when a temperature is set at which spinning is performed with nylon 6 in the above relative viscosity range, the difference in melt viscosity decreases, hence, cross-sectional formability can be stabilized, and the cross-sectional curvature can be set to 15% or less. The melt viscosity is more preferably 8,000 poise to 15,000 poise.

[0040] The melt viscosity of nylon at 240°C is preferably 200 poise to 2,000 poise. By setting the melt viscosity in such a range, when spinning is performed with the thermoplastic polyurethane described above, the difference in melt viscosity decreases, hence, the cross-sectional formability can be stabilized, and the cross-sectional curvature can be set to 15% or less. The melt viscosity is more preferably 300 poise to 1,500 poise.

[0041] It is possible to decrease the cross-sectional curvature by reducing the difference in melt viscosity between the thermoplastic polyurethane and the nylon 6 at the time of cross section formation. It is, however, impossible to measure actual melt viscosity in a spinning pack, thus the melt viscosity at 210°C for thermoplastic polyurethane, and the melt viscosity at 240°C for the nylon are taken as a standard. By using the thermoplastic polyurethane and the nylon 6 in such a range, the difference in melt viscosity can be sufficiently reduced at a preferable polymer temperature, which is described later.

[0042] The difference in melt viscosity between the thermoplastic polyurethane and nylon 6 at each polymer temperature is preferably 300 poise or less, more preferably 100 poise or less.

[0043] The polymer temperature of the thermoplastic polyurethane is preferably 235°C or higher and 245°C or lower. Here, the polymer temperature is a temperature before entering the spinning pack.

[0044] By setting the polymer temperature in such a range, a difference in melt viscosity from the nylon 6 can be reduced, cross-sectional formability can be stabilized, and the cross-sectional curvature can be set to 15% or less. The polymer temperature is more preferably 240°C or higher and 245°C or lower.

[0045] It is preferred that polymer temperature difference between the thermoplastic polyurethane and the nylon 6 is set within 10°C. Although a spinning temperature and the polymer temperature should be equal, due to variation in length of polymer pipe etc. of the spinning machine, decrease in polymer temperature from the polymer melting to the spinning pack should be considered to set an appropriate spinning temperature for the polymer temperature falling within such a range. By controlling the polymer temperature and the polymer temperature difference in such a range, heat transfer occurred between the thermoplastic polyurethane and the nylon 6 inside the spinning pack can be reduced, the temperature difference in a spinneret nozzle portion, which forms the conjugate cross section, decreases, the cross-sectional formability is stabilized, the cross-sectional curvature can be set to 15% or less, and the cross-sectional curvature CV value can be set to 0.40 or less.

[0046] The polymer temperature difference is preferably within 7°C. When the polymer temperature difference exceeds 10°C, heat transfer increases when a conjugate cross section is formed, the cross-sectional formability deteriorates, such as increase in curvature of an interface on the core portion side, and unstable curvature or the like, hence the cross-sectional curvature easily exceeds 15%, and the cross-sectional curvature CV value easily exceeds 0.40.

[0047] For example, under the melting conditions described in Patent Literature 1 and Patent Literature 2, the spinning temperature difference between the thermoplastic polyurethane and the nylon 6 is 20°C, namely the polymer temperature difference exceeds 10°C, and hence the cross-sectional curvature and the cross-sectional curvature CV value cannot be set in such a range.

[0048] Spinneret surface temperature difference is preferably within 5°C. Here, the spinneret surface temperature is a value obtained by measuring the temperature at the spinneret center and three outside locations and calculating a difference between a maximum value and a minimum value. By setting the spinneret surface temperature difference in such a range, the cross-sectional curvature CV value can be set to 0.40 or less.

[0049] The eccentric sheath-core conjugate fiber of the present invention is preferably used in fabric and clothing. A fabric type can be selected depending on the purpose, such as a woven fabric, a knitted fabric, or the like, as well as clothing. In addition, the clothing can be used as various clothing articles such as stockings, an innerwear, and a sportswear.

[0050] The eccentric sheath-core conjugate fiber of the present invention is preferably used in the stockings in which it is used in at least a part of a leg portion. Here, the stockings are stockings products including a pantyhose, long stockings, and short stockings. The leg portion refers to, for example in the pantyhose, the area from a garter portion to toes.

[0051] A knitting machine of the stockings is not particularly limited, and a usual sock knitting machine can be used. For example, knitting may be performed with a usual method in which eccentric sheath-core conjugate yarn of the present invention is supplied and knitted using a two-port or four-port yarn feeding sock knitting machine. Examples of the stockings include a Zocchi type stockings produced by supplying and knitting only the eccentric sheath-core conjugate yarn of the present invention or interknitted type stockings produced by alternately supplying and knitting a covering yarn, in which an elastic yarn as a core is wound by a covered yarn once or twice, and the eccentric sheath-core conjugate fiber of the present invention.

EXAMPLES

[0052] Hereinafter, the present invention is described specifically by referring to Examples. A measurement method and the like of characteristic values in the Examples are as follows.

(1) Sulfuric acid relative viscosity of nylon 6

[0053] 0.25 g of a nylon 6 chip sample was dissolved to be 1 g per 100 mL of sulfuric acid having a concentration of 98% by weight, and flow time (T1) at 25°C was measured using an Ostwald viscometer. Subsequently, fall time (T2) of only sulfuric acid having a concentration of 98% by weight was measured. A ratio of T1 to T2, namely, T1/T2, was taken as a sulfuric acid relative viscosity.

(2) Molecular weight (Mw, Mz/Mw) determination of thermoplastic polyurethane

[0054] 5 mL of a measurement solvent (0.05 M of lithium bromide added dimethyl formamide) was added to 10 mg of the thermoplastic polyurethane chip sample, and the mixture was stirred at room temperature for about 60 minutes. Thereafter, filtration was performed using a 0.45 µm membrane filter. Each molecular weight of the purified sample was determined under the following conditions.

Device: Gel permeation chromatograph GPC

Detector: Differential refractive index detector RI (RI-8020 type manufactured by Tosoh Corporation, sensitivity 32)

Column: one TSKgel α-M and one α-3000 (φ 7.8 mm × 30 cm, manufactured by Tosoh Corporation)

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Solvent: 0.05 M of lithium bromide added dimethyl formamide

Flow rate: 0.8mL/min

Column temperature: 0.2mL

Injection amount: 0.2mL

5 Standard sample: Monodispersed polystyrene manufactured by Tosoh Corporation

Data processing: GPC data processing system manufactured by TRC

(3) Melt viscosity

10 **[0055]** Melt viscosity was measured using "Flow Tester" CFT-500 manufactured by Shimadzu Corporation under conditions of die: 1.0 mm ϕ $\times$ 1.0 mm, plunger area: 1 cm², temperature: 210°C (thermoplastic polyurethane), 240°C (nylon 6), time: 4 minutes, load: 200 N, sample amount: 1 g.

(4) Fineness

15 **[0056]** A fiber sample was set in a counter reel of 1.125 m/cycle, the counter reel was rotated 200 cycles to produce a loop-shaped reel, the reel was dried with a hot air drier (105°C $\pm$ 2°C $\times$ 60 minutes) and then weighed with scales, and fineness was calculated from a value obtained by multiplying the reel weight by an official moisture rate. The sheath-core conjugate yarn had an official moisture rate of 4.5%.

(5) Strength and elongation

20 **[0057]** The fiber sample was measured by "TENSILON" (registered trademark), UCT-100 manufactured by Orientech Co., Ltd. under constant rate of specimen extension conditions shown in JIS L1013 (Testing methods for man-made filament yarns, 2010). The elongation was determined based on the elongation at a point that exhibited maximum strength in a tensile strength-elongation curve. Strength was a value obtained by dividing the maximum strength by fineness. The measurement was performed 10 times, and an average value was taken as the strength and elongation.

(6) Cross-sectional curvature

30 A. Photographing of cross-sectional photograph

35 **[0058]** An embedding agent containing paraffin, stearic acid, and ethyl cellulose was dissolved, the fiber is introduced into the embedding agent and solidified by leaving it at room temperature, the raw yarn in the embedding agent was cut in a cross-sectional direction, the fiber cross section was photographed with a CCD camera (CS5270) manufactured by Tokyo Electronics, Co., Ltd., and the photograph was printed out at 1500 times with a color video processor (SCT-CP710) manufactured by Mitsubishi Electric Corporation.

B. Measurement of cross-sectional curvature

40 **[0059]** Cross sections of all filaments of four eccentric sheath-core conjugate fibers were measured separately in the following procedures (a) to (e), and an average value thereof was taken as the cross-sectional curvature. The following is described with reference to Fig. 2.

- 45 a) A tangent line A is drawn at a point (point a) where a conjugate interface of the thermoplastic polyurethane and a polyamide is the most convex on the fiber cross section.
- b) A line B connecting two points (point b-1 and point b-2) where an inner diameter of the core portion is maximum is drawn parallel to the line A.
- 50 c) A line C connecting the point a and a middle point (point b-3) of the two points (point b-1 and point b-2) where the inner diameter of the core portion is maximum is drawn (extended to a fiber surface).
- d) An intersection point of the line C and the fiber surface nearer to the point a is set as point c, and the other intersection point of the line C and the fiber surface is set as point d.
- e)

55 Cross-sectional curvature = (length between point a-point b-3/length between point c-point d)/100

(7) Cross-sectional curvature CV value

[0060] The cross-sectional curvature of all the filaments of the four eccentric sheath-core conjugate fibers were measured and a standard deviation thereof was divided by an average value thereof. The resulting value was taken as the cross-sectional curvature CV value.

Cross-sectional curvature CV value = standard deviation value σ of cross-sectional curvature / average value of cross-sectional curvature

(8) Stretch and elongation rate

[0061] A stretch and elongation rate was determined by a formula shown below according to JIS L1090 (Testing methods for synthetic filament stretch yarns), Item 5.7, method C (simple method).

$$\text{Stretch and elongation rate (\%)} = [(L1 - L0)/L0] \times 100\%$$

L0: A reel length resulting from the following: a fiber reel was subjected to 90°C hot water treatment over 20 minutes while a load of 0.0018 cN/dtex was hung on the fiber reel and the reel was air dried whole day and night.

L1: A reel length resulting from the followings: L0 load was removed after L0 measurement and a load of 0.09 cN/dtex was hung for 30 seconds.

(9) Stockings production method

[0062] The four eccentric sheath-core conjugate fibers were used as yarns for a leg portion, and knitted into a jersey stitch with a Super 4 sock knitting machine (number of needles: 400) manufactured by Nagata Seiki Co., Ltd. to obtain stocking material.

[0063] Next, presetting was sequentially performed with 90°C steam and 100°C pressurized steam while the material was hung, and then a crotch portion and a toe portion were sewn.

[0064] After sufficiently washing and removing an oil agent of the fiber, the product was dyed to beige, a typical color of a pantyhose, and subjected to a fabric softener treatment at 95°C for 40 minutes, and then it was placed on an usual leg form to perform a final set at 110°C for 15 seconds to obtain the stockings.

(10) Appearance quality evaluation of stockings

[0065] The stockings produced in the above (9) were evaluated in four grades based on the following criteria, and C or above was set as "pass".

A: High appearance quality without streak.

B: Good appearance quality with almost no streaks.

C: No problem in appearance quality but some streaks.

D: Low appearance quality where streaks can be clearly recognized.

(11) Soft stretch evaluation of stockings

[0066] The stocking produced in the above (9) were evaluated in four grades based on the following criteria, and C or above was set as "pass".

A: Very good

B: Good

C: Slightly good

D: Poor

[Example 1]

[0067] A thermoplastic polyurethane (weight average molecular weight (M_w) = 114,000, M_z/M_w = 2.0, melt viscosity = 8,000 poise) in which a diisocyanate is diphenylmethane diisocyanate, a polyol includes two components of a polyester polyol and a polycarbonate polyol, and a chain extender is 1,4-butanediol was used as a core portion. As a heat resistant agent, each of 0.25% by weight of a hindered phenol-type stabilizer Irganox 1010 (manufactured by BASF Japan) and 0.25% by weight of Irganox 1330 (manufactured by BASF Japan) were added upon polymerization.

[0068] Then, nylon 6 having sulfuric acid relative viscosity of 2.20 was used as a sheath portion.

[0069] A thermoplastic polyurethane chip was melted at a spinning temperature (set value) of 242°C, and a nylon 6 chip was melted at a spinning temperature (set value) of 255°C, respectively. Polymer temperatures (measured value) before entering a spinning pack were: the thermoplastic polyurethane: 238°C; the nylon 6: 246°C. Melt discharging was performed at a weight ratio of the core portion thermoplastic polyurethane/the sheath portion nylon 6 of 50/50 using an eccentric sheath-core conjugate spinneret (round hole, 8 holes). The spinneret has a spinneret surface temperature of an average value of 226°C and a difference of 1.7°C.

[0070] Yarns discharged from the spinneret were cooled and solidified with a yarn cooling device, supplied with an oil agent (oil supply), and wound at 600 m/min. Then, the yarns were stretched by 4.29 times with a stretching machine, and a one-filament eccentric sheath-core conjugate monofilament of 18 dtex was wound on a bobbin and eight filaments were obtained. The strength of the yarn was 3.8 cN/dtex, and the elongation was 44%. The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 8.0%, a cross-sectional curvature CV value of 0.20, and a stretch and elongation rate of 115%.

[0071] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a good appearance quality with almost no streaks (B). Soft stretchability was also good (B).

[Example 2]

[0072] Spinning was performed in the same method as in Example 1 except that the weight average molecular weight (M_w) of the thermoplastic polyurethane was 130,000 (M_z/M_w = 2.0, melt viscosity = 9,500 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0073] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 10.0%, a CV value of 0.20, and a stretch and elongation rate of 105%.

[0074] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a good appearance quality with almost no streaks (B). Soft stretchability was also good (B).

[Example 3]

[0075] Spinning was performed in the same method as in Example 1 except that the weight average molecular weight (M_w) of the thermoplastic polyurethane was 150,000 (M_z/M_w = 2.5, melt viscosity = 11,500 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0076] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 12.5%, a CV value of 0.30, and a stretch and elongation rate of 100%.

[0077] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed no problem in the appearance quality but some streaks (C). The soft stretchability was also slightly good (C).

[Example 4]

[0078] Spinning was performed in the same method as in Example 1 except that the weight average molecular weight (M_w) of the thermoplastic polyurethane was 180,000 (M_z/M_w = 2.8, melt viscosity = 14,000 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0079] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 14.5%, a CV value of 0.35, and a stretch and elongation rate of 93%.

[0080] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed no problem in the appearance quality but some streaks (C). The soft stretchability was also slightly good (C).

[Example 5]

[0081] Spinning was performed in the same method as in Example 1 except that the weight average molecular weight (M_w) of the thermoplastic polyurethane was 80,000 (M_z/M_w = 1.9, melt viscosity = 5,000 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0082] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 5.0%, a CV value of 0.18, and a stretch and elongation rate of 120%.

[0083] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a high appearance quality without a stripe (A). The soft stretchability was also very good (A).

[Example 6]

[0084] A thermoplastic polyurethane chip was melted at a spinning temperature (set value) of 247°C, and a nylon 6 chip was melted at a spinning temperature (set value) of 255°C, respectively, and the polymer temperatures (measured value) before entering the spinning pack were: the thermoplastic polyurethane: 240°C; the nylon 6: 246°C. The spinneret has a spinneret surface temperature of an average value of 227°C and a difference of 1.8°C. Spinning was performed in the same method as in Example 1 except that the melting conditions of the thermoplastic polyurethane were changed, and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0085] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 5.0%, a CV value of 0.18, and a stretch and elongation rate of 120%.

[0086] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a high appearance quality without a streak (A). The soft stretchability was also very good (A).

[Example 7]

[0087] A thermoplastic polyurethane chip was melted at a spinning temperature (set value) of 252°C, and a nylon 6 chip was melted at a spinning temperature (set value) of 255°C, respectively. Polymer temperatures (measured value) before entering a spinning pack were: the thermoplastic polyurethane: 244°C; the nylon 6: 246°C. The spinneret has spinneret surface temperature of an average value of 229°C and a difference of 0.8°C. Spinning was performed in the same method as in Example 1 except that the melting conditions of the thermoplastic polyurethane were changed, and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0088] The obtained eccentric sheath-core conjugate monofilament raw yarn had cross-sectional curvature of 3.0%, a CV value of 0.15, and a stretch and elongation rate of 125%.

[0089] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a high appearance quality without a streak (A). The soft stretchability was also very good (A).

[Example 8]

[0090] Spinning was performed in the same method as in Example 7 except that the weight average molecular weight (Mw) of the thermoplastic polyurethane was 80,000 (Mz/Mw = 1.9, melt viscosity = 5,000 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0091] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 1.0%, a CV value of 0.10, and a stretch and elongation rate of 130%.

[0092] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a high appearance quality without a streak (A). The soft stretchability was also very good (A).

[Example 9]

[0093] Spinning was performed in the same method as in Example 8 except that the sulfuric acid relative viscosity of the nylon 6 was 2.00 (melt viscosity = 300 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0094] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 1.0%, a CV value of 0.10, and a stretch and elongation rate of 120%.

[0095] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a high appearance quality without a streak (A). The soft stretchability was also very good (A).

[Example 10]

[0096] Spinning was performed in the same method as in Example 7 except that the sulfuric acid relative viscosity of the nylon 6 was 2.30 (melt viscosity = 1500 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0097] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 10.0%, a CV value of 0.30, and a stretch and elongation rate of 103%.

[0098] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a good appearance quality with almost no streaks (B). Soft stretchability was also good (B).

[Comparative Example 1]

[0099] Spinning was performed in the same method as in Example 1 except that the weight average molecular weight (Mw) of the thermoplastic polyurethane was 250,000 ($M_z/M_w = 3.1$, melt viscosity = 21,000 poise), and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0100] The obtained raw yarn had cross-sectional curvature of 19.0%, a CV value of 0.45, and a stretch and elongation rate of 80%. That is, it can be seen that curve of an interface on the core portion side is large, the coil shaped crimp is minute and not uniform, and the crimp properties are poor.

[0101] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a low appearance quality where streaks can be clearly recognized (D). The soft stretchability was also poor (D).

[Comparative Example 2]

[0102] A thermoplastic polyurethane chip was melted at a spinning temperature (set value) of 236°C, and a nylon 6 chip was melted at a spinning temperature (set value) of 255°C, respectively. Polymer temperatures (measured value) before entering a spinning pack were: the thermoplastic polyurethane: 230°C; the nylon 6: 246°C. The spinneret has spinneret surface temperature of average value of 225°C and a difference of 6.2°C. Spinning was performed in the same method as in Example 1 except that the melting conditions of the thermoplastic polyurethane were changed, and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0103] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 23.0%, a CV value of 0.55, and a stretch and elongation rate of 80%. That is, it can be seen that curve of an interface on the core portion side is large, the coil shaped crimp is minute and not uniform, and the crimp properties are poor.

[0104] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a low appearance quality where streaks can be clearly recognized (D). The soft stretchability was also poor (D).

[Comparative Example 3]

[0105] A thermoplastic polyurethane chip was melted at a spinning temperature (set value) of 230°C, and a nylon 6 chip was melted at a spinning temperature (set value) of 250°C, respectively. Polymer temperatures (measured value) before entering a spinning pack were: the thermoplastic polyurethane: 225°C; the nylon 6: 242°C. The spinneret has spinneret surface temperature of an average value of 224°C and a difference of 7.5°C. Spinning was performed in the same method as in Example 1 except that the melting conditions of the thermoplastic polyurethane were changed, and one-filament eccentric sheath-core conjugate monofilament of 18 dtex was obtained.

[0106] The obtained eccentric sheath-core conjugate monofilament had cross-sectional curvature of 24.5%, a CV value of 0.55, and a stretch and elongation rate of 80%. That is, it can be seen that curve of an interface on the core portion side is large, the coil shaped crimp is minute and not uniform, and the crimp properties are poor.

[0107] The stockings produced using the obtained eccentric sheath-core conjugate monofilament showed a low appearance quality where streaks can be clearly recognized (D). The soft stretchability was also poor (D).

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5
Core portion	Polymer	Thermoplastic polyurethane	Thermoplastic polyurethane	Thermoplastic polyurethane	Thermoplastic polyurethane
	Mw	114,000	130,000	150,000	180,000
	Mz/Mw	2.0	2.0	2.5	2.8
	Melt viscosity (poise)	8,000	9,500	11,500	14,000
Sheath portion	Polymer	Nylon 6	Nylon 6	Nylon 6	Nylon 6
	Sulfuric acid relative viscosity	2.20	220	2.20	2.20
	Melt viscosity (poise)	550	550	550	550
Molten portion	Core side: Spinning temperature (°C)	242	242	242	242
	Sheath side: Spinning temperature (°C)	255	255	255	255
Merging portion	Core side: Polymer temperature (°C)	238	238	238	238
	Sheath side: Polymer temperature (°C)	246	246	246	246
	Polymer temperature difference (°C)	8	8	8	8
	Spinneret surface temperature (°C)	226	226	226	226
Discharging portion	Spinneret surface temperature difference (°C)	1.7	1.7	1.7	1.7

(continued)

		Example 1	Example 2	Example 3	Example 4	Example 5
Yarn properties	Strength (cN/dtex)	3.8	3.9	4.0	4.0	4.1
	Elongation (%)	44	43	46	44	45
	Cross-sectional curvature (%)	8.0	10.0	12.5	14.5	5.0
	Cross-sectional curvature CV value	0.20	0.20	0.30	0.35	0.18
	Stretch and elongation rate (%)	115	105	100	93	120
Stocking properties	Appearance quality	B	B	C	C	A
	Soft stretch	B	B	C	C	A

[Table 2]

		Example 6	Example 7	Example 8	Example 9	Example 10
Core portion	Polymer	Thermoplastic polyurethane	Thermoplastic polyurethane	Thermoplastic polyurethane	Thermoplastic polyurethane	Thermoplastic polyurethane
	Mw	114,000	114,000	80,000	80,000	114,000
	Mz/Mw	2.0	2.0	1.9	1.9	2.0
	Melt viscosity (poise)	8,000	8,000	5,000	5,000	8,000
Sheath portion	Polymer	Nylon 6	Nylon 6	Nylon 6	Nylon 6	Nylon 6
	Sulfuric acid relative viscosity	2.20	2.20	2.20	2.00	2.30
	Melt viscosity (poise)	550	550	550	300	1500
Molten portion	Core side: Spinning temperature (°C)	247	252	252	252	252
	Sheath side: Spinning temperature (°C)	255	255	255	255	255
Merging portion	Core side: Polymer temperature (°C)	240	244	244	244	244
	Sheath side: Polymer temperature (°C)	246	246	246	246	246
	Polymer temperature difference (°C)	6	2	2	2	2
Discharging portion	Spinneret surface temperature (°C)	227	229	229	229	229
	Spinneret surface temperature difference (°C)	1.3	0.8	0.8	0.8	0.8

(continued)						
		Example 6	Example 7	Example 8	Example 9	Example 10
Yarn properties	Strength (cN/dtex)	4.0	4.2	4.2	3.5	3.9
	Elongation (%)	46	43	45	44	47
	Cross-sectional curvature (%)	5.0	3.0	1.0	1.0	10.0
	Cross-sectional curvature CV value	0.18	0.15	0.10	0.10	0.30
	Stretch and elongation rate (%)	120	125	130	120	103
Stocking properties	Appearance quality	A	A	A	A	B
	Soft stretch	A	A	A	A	B

[Table 3]

		Comparative Example 1	Comparative Example 2	Comparative Example 3
5 10	Core portion	Polymer	Thermoplastic polyurethane	Thermoplastic polyurethane
		Mw	250,000	114,000
		Mz/Mw	3.1	2.0
		Melt viscosity (poise)	21,000	8,000
15	Sheath portion	Polymer	Nylon 6	Nylon 6
		Sulfuric acid relative viscosity	2.20	2.20
		Melt viscosity (poise)	550	550
20	Molten portion	Core side: Spinning temperature (°C)	242	236
		Sheath side: Spinning temperature (°C)	255	250
25 30	Merging portion	Core side: Polymer temperature (°C)	238	230
		Sheath side: Polymer temperature (°C)	246	242
		Polymer temperature difference (°C)	8	17
35	Discharging portion	Spinneret surface temperature (°C)	226	225
		Spinneret surface temperature difference (°C)	1.7	7.5
40 45	Yarn properties	Strength (cN/dtex)	3.6	4.0
		Elasticity (%)	49	43
		Cross-sectional curvature (%)	19	23
		Cross-sectional curvature CV value	0.45	0.55
		Stretch and elongation rate (%)	80	80
45	Stocking properties	Appearance quality	D	D
		Soft stretch	D	D

[0108] Although the present invention has been described in detail using specific embodiments, it will be apparent to those skilled in the art that various modifications and variations are possible without departing from the spirit and scope of the present invention. The present application is based on Japanese Patent Application No. 2017-123316 filed on June 23, 2017, and the contents thereof are incorporated herein by reference.

Reference Signs

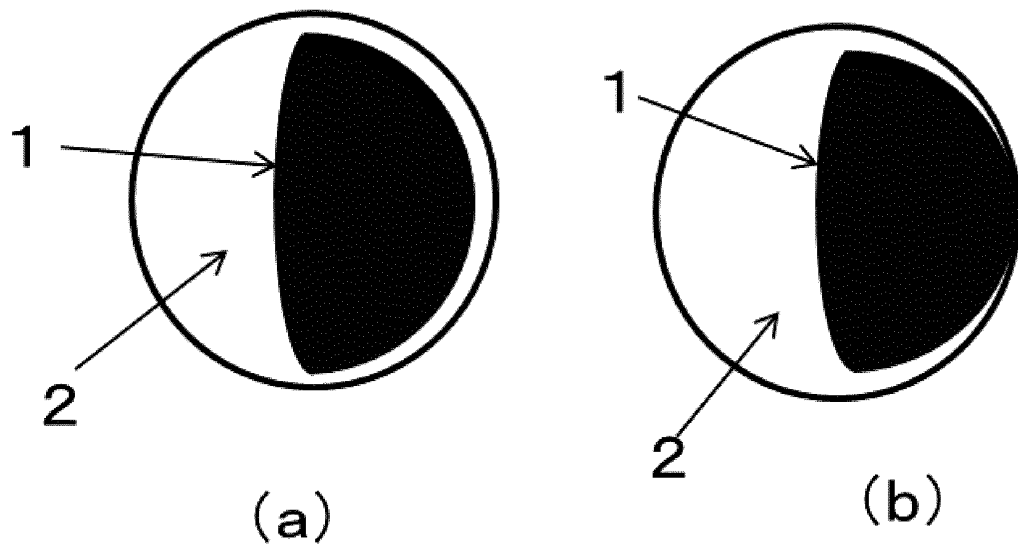
[0109]

- 1: Thermoplastic polyurethane
- 2: Nylon 6

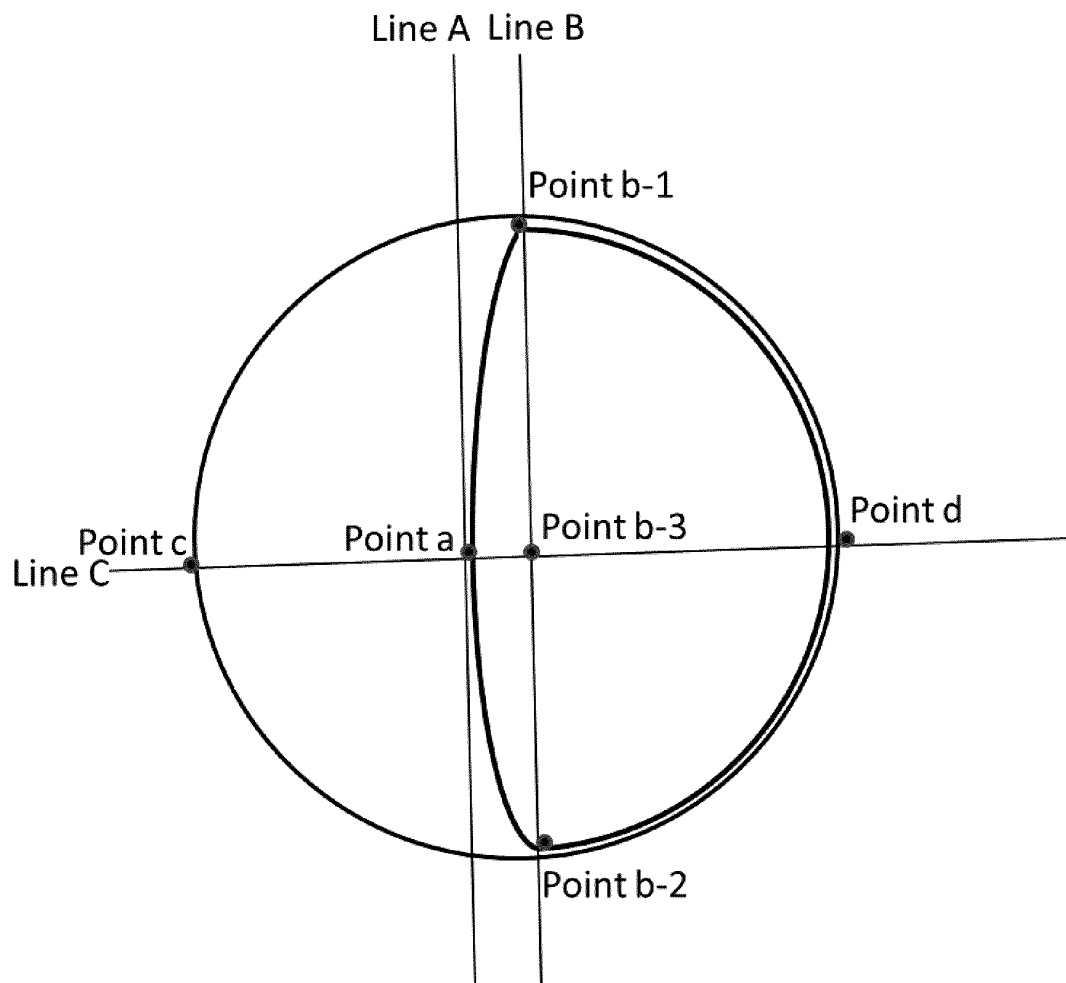
5 **Claims**

- 1. An eccentric sheath-core conjugate fiber comprising a core component, which is a thermoplastic polyurethane, and a sheath component, which is nylon 6, wherein the eccentric sheath-core conjugate fiber has cross-sectional curvature of 15% or less and a cross-sectional curvature CV value of 0.40 or less.
- 2. The eccentric sheath-core conjugate fiber according to claim 1, having a stretch and elongation rate of 90% or more.
- 3. A woven/knitted fabric comprising the eccentric sheath-core conjugate fiber according to claim 1 or 2 in at least a part thereof.
- 4. Stockings comprising the eccentric sheath-core conjugate fiber according to claim 1 or 2 in at least a part of a leg portion thereof.

[Fig. 1]



[Fig. 2]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/023038

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. D01F8/12(2006.01)i, A41B11/14(2006.01)i, D01F8/16(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)

Int.Cl. D01F8/00-8/18, A41B11/00-11/14, D04B1/00-1/28, 21/00-21/20

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 3-206124 A (TORAY INDUSTRIES, INC.) 09 September 1991, claim 1, page 1, right column, lines 5-10, page 2, lower left column, lines 6-15, page 3, lower left column, lines 11-16, page 4, upper left column, line 14 to upper right column, line 12 (Family: none)	1-4
A	JP 2-53925 A (TORAY INDUSTRIES, INC.) 22 February 1990, claims 1, 2, page 2, upper left column, lines 4-9, page 2, upper right column, lines 5-10, page 2, lower left column, pp. 15-20 (Family: none)	1-4
A	JP 2012-36541 A (SEIREN CO., LTD.) 23 February 2012, paragraphs [0053]-[0055] (Family: none)	1-4

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

 Date of the actual completion of the international search
 06 August 2018 (06.08.2018)

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2080616 A [0006]
- JP 7091693 B [0006]
- JP 2017123316 A [0108]