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(71) Applicant: **Kuraray Trading Co., Ltd.**
Osaka-shi, Osaka 530-8611 (JP)

(72) Inventors:
- **IKEDA, Takayuki**
  Kurashiki-shi, Okayama 713-8550 (JP)
- **NAKATSUKA, Hitoshi**
  Saijo-shi, Ehime 793-8585 (JP)
- **KAWAKADO, Shinya**
  Kurashiki-shi, Okayama 713-8550 (JP)
- **YAMASAKI, Kohei**
  Kurashiki-shi, Okayama 713-8550 (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) SEA-ISLAND TYPE COMPOSITE MULTIFILAMENT, ULTRAFINE MULTIFILAMENT, AND ULTRAFINE FIBER STRUCTURE

(57) Provided are a sea-island type composite multifilament which includes a thermoplastic elastomer resin as an island component, and an ultrafine multifilament prepared from such a sea-island type composite multifilament. The sea-island type composite multifilament includes an island component and a sea component. The island component includes a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less. The sea component includes a water-soluble or easily alkali-soluble thermoplastic resin (B). The sea-island type composite multifilament has an average single island diameter of 8000 nm or less.

EP 4 279 644 A1

Description

CROSS REFERENCE TO THE RELATED APPLICATION

[0001] This application is based on and claims Convention priority to Japanese patent application No. 2021-004876, filed January 15, 2021 in Japan, the entire disclosure of which is herein incorporated by reference as a part of this application.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a sea-island type composite multifilament which comprises a thermoplastic elastomer resin as an island component, and an ultrafine fiber which comprises an ultrafine multifilament prepared from such a sea-island type composite multifilament.

[0003] A sea-island type composite multifilament can be formed as a composite multifilament comprising, as a sea component thereof, a resin which can be dissolved and removed therefrom. Thereafter, ultrafine fibers can be produced by subjecting the sea-island type composite multifilament to remove the sea component therefrom.

[0004] For example, Patent Document 1 (JP Laid-open Patent Publication No. 2014-101613) discloses an ultrafine fiber having an average single filament diameter of 10 to 2500 nm and a tensile strength of 4.5 cN/dtex or more, wherein the ultrafine fiber is obtained by dissolving a sea component in a sea-island type composite fiber to be removed therefrom, the sea-island type composite fiber satisfying all of the following conditions:

(A) the sea-island type composite fiber comprises a sea component and an island component at a composite mass ratio (sea: island) in the range of from 40: 60 to 20: 80;
(B) the sea-island type composite fiber has a melt viscosity ratio (sea / island) of the sea component to the island component in the range of from 0.2 to 1.0;
(C) the sea-island type composite fiber is prepared by melting the sea component and the island component, extruding the melts from a spinneret, and taking up extruded filaments at a spinning rate of 400 to 2000 m/min;
(D) the sea-island type composite fiber is obtained by being subjected to preheating on preheat rollers, drawing at a drawing ratio of 3.0 to 6.0, and heat-setting on heat-set rollers, before being wound; and
(E) the sea-island type composite fiber has a residual elongation of 5 to 30% by drawing.
[Patent Document 1] JP Laid-open Patent Publication No. 2014-101613

SUMMARY OF THE INVENTION

[0005] While a polyester ultrafine fiber with an excellent strength can be formed in Patent Document 1, the ultrafine fibers slip relative to each other, thereby resulting in poor grip performance. Hence, where the ultrafine fibers are used for anti-slip application to, for example, innerwear or gloves, a frictional or sticking effect provided by this polyester ultrafine fiber may be insufficient.

[0006] Therefore, an object of the present invention is to provide an ultrafine multifilament that exhibits excellent grip performance, a sea-island type composite multifilament from which such an ultrafine multifilament can be formed, and production methods therefor as well as a fiber structure.

[0007] As a result of intensive studies conducted by the inventors of the present invention in an attempt to achieve the above object, the inventors of the present invention found that the use of a thermoplastic elastomer resin having a hardness in a specific range as an island component of a sea-island type composite multifilament would be effective in obtaining an ultrafine multifilament that exhibits advantageous grip performance. However, they also found that preparation of a sea-island type composite multifilament comprising a thermoplastic elastomer resin as an island component could not carried out in the same manner as a sea-island type composite multifilament comprising a non-elastomer resin as an island component, due to the high stretchability of a thermoplastic elastomer resin, and therefore tackled this as a new problem.

[0008] Upon further studies, they have found that a sea-island type composite multifilament which comprises a thermoplastic elastomer resin as an island component can be prepared by lowering the single filament fineness of the sea-island type composite multifilament while decreasing the number of the islands in the sea-island type composite multifilament, and that an ultrafine multifilament comprising a thermoplastic elastomer can be successfully produced by removing the sea component from such an island type composite multifilament. They have further found that, where the thermoplastic elastomer resin has a hardness in a specific range, the ultrafine multifilament exhibits excellent grip performance that was hitherto not achieved, and thus the inventors finally completed the invention.

[0009] Accordingly, the present invention may encompass the following aspects.

[0010] Aspect 1: a sea-island type composite multifilament comprising an island component and a sea component,

the island component comprising a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less (preferably 58 or less, more preferably 55 or less, further preferably 53 or less, and even more preferably 50 or less), or a Rockwell hardness (R scale) of 70 or less (preferably 65 or less, and further preferably 60 or less), the sea component comprising a water-soluble or easily alkali-soluble thermoplastic resin (B), and the sea-island type composite multifilament having an average single island diameter of 8000 nm or less (preferably 6000 nm or less, and more preferably 4000 nm or less).

[0011] Aspect 2: the sea-island type composite multifilament of Aspect 1, wherein the thermoplastic resin (B) of the sea component comprises a modified polyvinyl alcohol-based polymer in which a unit derived from an α-olefin and/or a vinyl ether is contained in a polyvinyl alcohol-based polymer moiety.

[0012] Aspect 3: the sea-island type composite multifilament of Aspect 1 or 2, wherein the number of islands in the sea-island type composite multifilament is from 3 to 200 (preferably from 5 to 100, more preferably from 6 to 80, and further preferably from 7 to 60), and the sea-island type composite multifilament has a composite mass ratio (sea component: island component) between the sea component and the island component of from 20:80 to 70:30 (preferably from 25:75 to 70:30, and further preferably from 30:70 to 60:40).

[0013] Aspect 4: the sea-island type composite multifilament of any one of Aspects 1 to 3, wherein the thermoplastic elastomer resin (A) comprises a polyamide-based elastomer resin or a polyester-based elastomer resin.

[0014] Aspect 5: a fiber structure comprising, at least in part thereof, a sea-island type composite multifilament of any one of Aspects 1 to 4 and/or a cut fiber thereof.

[0015] Aspect 6: an ultrafine multifilament comprising a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less, the ultrafine multifilament having a coefficient of fiber-to-metal dynamic friction of 0.30 or more (preferably 0.33 or more, and more preferably 0.36 or more).

[0016] Aspect 7: the ultrafine multifilament of Aspect 6, wherein the ultrafine multifilament has a single filament fineness of from 0.005 to 0.5 dtex (preferably from 0.010 to 0.4 dtex, and more preferably from 0.015 to 0.3 dtex).

[0017] Aspect 8: an ultrafine fiber structure comprising, at least in part thereof, an ultrafine multifilament of Aspect 6 or 7 and/or a cut fiber thereof.

[0018] Aspect 9: the ultrafine fiber structure of Aspect 8, wherein the ultrafine fiber structure comprises a woven fabric or a knitted fabric.

[0019] Aspect 10: a process for producing an ultrafine multifilament, the process comprising at least dissolving a thermoplastic resin (B) to be removed from a sea-island type composite multifilament of any one of Aspects 1 to 4,

[0020] Aspect 11: a process for producing an ultrafine fiber structure, the process comprising at least dissolving a thermoplastic resin (B) to be removed from a fiber structure of Aspect 5.

[0021] It should be noted that any combinations of at least two features disclosed in the claims and/or the specification and/or the drawings should also be construed as encompassed by the present invention. Especially, any combinations of two or more of the claims should also be construed as encompassed by the present invention.

[0022] A sea-island type composite multifilament according to the present invention is prepared by subjecting a thermoplastic elastomer resin having a hardness in a specific range as a resin constituting an island component (which will hereinafter be referred to at times as an island component resin) along with a resin which can be easily removed by water or alkali as a resin constituting a sea component (which will hereinafter be referred to at times as a sea component resin) to a conjugate spinning process. In this way, ultrafine spinnability of the thermoplastic elastomer resin can be carried out in an efficient manner.

[0023] Further, an ultrafine multifilament according to the present invention comprises such a thermoplastic elastomer resin and therefore has a high coefficient of dynamic friction, thereby exhibiting improved grip performance.

DESCRIPTION OF EMBODIMENTS

Sea-island type Composite Multifilament

[0024] The sea-island type composite multifilament according to the present invention comprises a resin constituting an island component and a resin constituting a sea component. The resin constituting an island component comprises a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less. The resin constituting a sea component comprises a water-soluble or easily alkali-soluble thermoplastic resin (B).

[0025] The sea-island type composite multifilament can have a small average single island diameter. The sea-island type composite multifilament may have an average single island diameter of 8000 nm or less, preferably 6000 nm or less, and more preferably 4000 nm or less. While no specific lower limit is given for the average single island diameter, an average single island diameter of, for example, 500 nm or more may be used as the lower limit. The average single island diameter in this context is determined in accordance with a procedure described in the Examples section below.

Island Component Resin

[0026] The island component resin comprises a thermoplastic elastomer resin (A) having a hardness in a specific range. The selection of an appropriate standard to determine the hardness of the thermoplastic elastomer resin (A) is hardness-dependent: that is, among a Shore A hardness, a Shore D hardness, and a Rockwell hardness (R scale), (i) a measurement based on the Rockwell hardness (R scale) is used when the Rockwell hardness (R scale) has the highest value; (ii) a measurement based on the Shore D hardness is used when the Rockwell hardness (R scale) is less than 50; and (iii) a measurement based on the Shore A hardness is used when the Shore D hardness is 40 or less.

[0027] The hardness of the island component resin suffices at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less: for example, the Shore D hardness of the island component resin does not have to be 60 or less, if the Rockwell hardness (R scale) of the island component resin is 70 or less.

[0028] A Shore A hardness is a measurement of an indentation hardness by means of a durometer in accordance with JIS K 7215 and is determined by using a type A indenter (having a frustoconical tip, a tip diameter of 0.79 mm, and a cone angle of 35°). The Shore A hardness of the island component resin may be 90 or less, from the viewpoint of grip performance of an ultrafine multifilament derived therefrom. While no specific lower limit is given for the Shore A hardness to the extent that the effect of the present invention is not spoiled, a Shore A hardness of, for example, 20 or more and preferably 50 or more may be used as the lower limit.

[0029] A Shore D hardness is a measurement of an indentation hardness by means of a durometer in accordance with JIS K 7215 and is determined by using a type D indenter (having a conical tip, a tip diameter of 0.1 mm, and a cone angle of 30°). The Shore D hardness of the island component resin may be 60 or less, preferably 58 or less, more preferably 55 or less, further preferably 53 or less, and even more preferably 50 or less, from the viewpoint of grip performance of an ultrafine multifilament derived therefrom. While no specific lower limit is given for the Shore D hardness to the extent that the effect of the present invention is not spoiled, a Shore D hardness of, for example, 20 or more may be used as the lower limit.

[0030] A Rockwell hardness (R scale) is a measurement of an indentation hardness made in accordance with JIS Z 2245 and is determined by using a rigid ball having a diameter of 12.7 mm as an indenter. The Rockwell hardness (R scale) of the island component resin may be 70 or less, preferably 65 or less, and further preferably 60 or less, from the viewpoint of grip performance of an ultrafine multifilament derived therefrom. While no specific lower limit is given for the Rockwell hardness (R scale) to the extent that the effect of the present invention is not spoiled, a Rockwell hardness (R scale) of, for example, 50 or more may be used as the lower limit.

[0031] Examples of the thermoplastic elastomer resin may include a polyolefinic elastomer resin, a polyvinyl chloride-based elastomer resin, a polyurethane-based elastomer resin, a polystyrene-based elastomer resin, a polyester-based elastomer resin, and a polyamide-based elastomer resin. Among them, a polyamide-based elastomer resin and a polyester-based elastomer resin are preferable from the viewpoint of better handleability; a polyamide-based elastomer resin is preferable from the viewpoint of color fastness to washing.

[0032] The polyolefinic elastomer resin comprises a hard segment derived from a polyethylene and/or a polypropylene and a soft segment derived from an SEBS (styrene-ethylene-butylene-styrene) and/or an ethylcne/propylene copolymer.

[0033] The polyvinyl chloride-based elastomer resin comprises a hard segment derived from a crystalline polyvinyl chloride and a soft segment derived from an amorphous polyvinyl chloride and/or acrylonitrile.

[0034] The polyurethane-based elastomer resin comprises a hard segment derived from a low molecular weight glycol and a diisocyanate and a soft segment derived from a high molecular weight diol and a diisocyanate.

[0035] Examples of the low molecular weight glycol include $C_{1\text{-}10}$ diols such as ethylene glycol, 1,4-butanediol, and 1,6-hexanediol. Examples of the high molecular weight diol include a poly(l,4-butylene adipate), a poly(1,6-hexane adipate), a polycaprolactone, a polyethylene glycol, a polypropylene glycol, and a polyoxytetramethylene glycol. Examples of the diisocyanate include tolylene diisocyanate, 4,4-diphenylmethane diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate.

[0036] The polystyrene-based elastomer resin comprises a hard segment derived from a polystyrene and a soft segment derived from a polybutadiene, a polyisoprene, a hydrogenated poly butadiene, a polyethylene, a polypropylene and/or the like. Examples of the polystyrene-based elastomer resin include an SBS (styrene/butadiene/styrene block copolymer), an SIS (styrene/isoprene/styrene block copolymer). an SEBS (styrene/ethylene/butadiene/styrene block copolymer), and an SEPS (styrene/ethylene/propylene/styrene block copolymer). For the polystyrene-based elastomer resin, a resin having a hardness in a predetermined range can be selected from polystyrene-based elastomer resins on the market such as, for example, "SEPTON" available from KURARAY CO., LTD. and "HYBRAR" available from KURARAY CO., LTD.

[0037] The polyester-based elastomer resin comprises a hard segment derived from an aromatic polyester resin component and a soft segment derived from an aliphatic polyether and/or an aliphatic polyester. For the polyester-based elastomer resin, a resin having a hardness in a predetermined range can be selected from polyester-based elastomer

resins on the market such as, for example, "SKYPEL" available from SK chemical, "HYTREL" available from DU PONT-TORAY CO., LTD., and "PELPRENE" available from Toyobo Co., Ltd.

[0038] Examples of the polyamide-based elastomer resin may comprise a polyether-block polyamide, a polyester-block polyamide, and a polyester-ether-block polyamide, each comprising a hard segment derived from a polyamide-based elastomer resin component and a soft segment derived from a polyether block and/or a polyester block.

[0039] The polyamide-based elastomer may comprise a hard segment derived from, for example, an aliphatic polyamide having 6 to 22 carbon atoms, and preferably an aliphatic polyamide having 9 to 20 carbon atoms. The aliphatic polyamide in this context means a polyamide which comprises at least one of repeating units represented by formulae (1) to (3) below and includes saturated aliphatic hydrocarbon groups as the hydrocarbon groups in the formulae.

$$-NH-R1-NH- \quad (1)$$

$$-C-(R2)_m-CO- \quad (2)$$

$$-NH-R3-CO- \quad (3)$$

[0040] In the formulae, R1, R2, and R3 are the same or different and represent a linear or branched, aliphatic hydrocarbon group having 1 to 22 carbon atoms, and in represents an integer of 0 or 1.

[0041] More specifically, for example, the polyether-block polyamide may comprise a hard segment derived from a polyamide 6, a polyamide 6/6, a polyamide 6/11, a polyamide 6/12, a polyamide 9, a polyamide 11, a polyamide 12, and/or the like and a soft segment derived from a polyethylene glycol, a polypropylene glycol, a polytetramethylene glycol and/or the like. For the polyamide-based elastomer resin, a resin having a hardness in a predetermined range can be selected from polyamide-based elastomer resins on the market such as, for example, "VESTAMID" and "DAIAMID" available from Daicel-Evonik, "PEBAX" available from ARKEMA, and "UBESTAXPA" available from Ube Industries, Ltd.

[0042] It should be noted that an amino group-containing color enhancer (color developing improver) may be combined with the polyamide-based elastomer resin, from the viewpoint of improved color development performance. The amino group-containing color enhancer at least contains an amino group and can impart a desired amino end group concentration to the polyamide-based elastomer resin when used in combination therewith. The amino group-containing color enhancer may have an amino end group concentration of, for example, from 100 to 2000 μeq/g, preferably from 125 to 2000 μeq/g, and more preferably from 200 to 1000 μeq/g.

[0043] The amino group-containing color enhancer can be combined with the polyamide-based elastomer resin at any proportion appropriate for the type of the amino group-containing color enhancer, to the extent that the properties of the polyamide-based elastomer resin are not spoiled. For example, the mass ratio of the polyamide-based elastomer resin to the amino group-containing color enhancer may be, for example, from 99/1 to 70/30, preferably from 98/2 to 75/25, and more preferably from 95/5 to 80/20, from the viewpoint of color development performance and compatibility.

[0044] Examples of the amino group-containing color enhancer may include a polyamide oligomer and an amino group-containing compound such as a multi-amine compound (e.g., a multi-amine compound having a linear aliphatic, alicyclic, or aromatic compound with 3 to 12 amino groups), from the viewpoint of improved color development performance of the resulting polyamide-based fiber without spoiling the properties of the polyamide-based elastomer resin.

[0045] The polyamide oligomer preferably comprises at least one of the repeating units represented by formulae (1) to (3) mentioned in the item of the polyamide-based elastomer resin. The at least one of the repeating units represented by formulae (1) to (3) may comprise a hydrocarbon group having 1 to 22 carbon atoms, examples of which may include a linear or branched, saturated aliphatic hydrocarbon group having 1 to 22 (preferably 6 to 20, and more preferably 9 to 18) carbon atoms, a linear or branched, saturated alicyclic hydrocarbon group having 6 to 22 (preferably 6 to 20, and more preferably 6 to 18) carbon atoms, and a linear or branched, aromatic hydrocarbon group having 6 to 22 (preferably 6 to 20, and more preferably 6 to 18) carbon atoms. Any one of these hydrocarbon groups may be substituted with given substituent(s) to the extent that the effect of the present invention is not spoiled.

[0046] Preferred examples of the polyamide oligomer may include a polyamide 6 oligomer, a polyamide 4/6 oligomer, a polyamide 6/6 oligomer, a polyamide 6/10 oligomer, a polyamide 6/11 oligomer, a polyamide 6/12 oligomer, a polyamide 9 oligomer, a polyamide 10 oligomer, a polyamide 11 oligomer, and a polyamide 12 oligomer.

[0047] It is preferred that the number of carbon atoms of a hydrocarbon group in a repeating unit in the polyamide oligomer be equivalent to the number of carbon atoms of a hydrocarbon group in a repeating unit in the polyamide-based elastomer resin, from the viewpoint of compatibility of the polyamide oligomer with the polyamide-based elastomer resin. For example, the number of carbon atoms of a hydrocarbon group in a repeating unit in the polyamide oligomer may be within the range of the number of carbon atoms in a repeating unit in the polyamide-based elastomer resin ± 3, preferably within the range of the number of carbon atoms in a repeating unit in the polyamide-based elastomer resin ± 2, and more preferably within the range of the number of carbon atoms in a repeating unit in the polyamide-based elastomer resin ± 1. It should be noted that, when the polyamide-based elastomer resin comprises a polyamide-based

elastomer, a hydrocarbon group in a repeating unit in the polyamide-based elastomer resin component within a hard segment of the polyamide-based elastomer preferably meets the above relations on behalf of a hydrocarbon group in the polyamide-based elastomer resin.

[0048] The polyamide oligomer may have a number-average molecular weight of, for example, from 500 to 10000, preferably from 500 to 9000, and more preferably from 1000 to 6000. The molecular weight of the polyamide oligomer in this context is determined in accordance with a procedure described in the Examples section below.

[0049] Where necessary, the island component resin may also comprise one or more various additives that is/are typically used in the art. Examples of the additives may include a heat stabilizer, an antioxidant, a light stabilizer, an ultraviolet absorber, an antistatic agent, a colorant (e.g., a coloring pigment), a lubricating agent, a plasticizer, an antibacterial agent, a fungicide, and an anti-odor agent. Further, the island component resin may additionally comprise a non-thermoplastic elastomer resin to the extent that the effect of the present invention is not spoiled.

[0050] The island component resin preferably has a melt viscosity at 240°C of from 600 to 3000 poise from the viewpoint of better spinnability (filament-forming property). A melt viscosity of more than 3000 poise of the island component resin can result in poor, high-speed spinnability during spinning. Meanwhile, a melt viscosity of less than 600 poise of the island component resin can result in poor productivity due to an increased chance of a filament breakage during spinning process and can also result in a low strength of the resulting fiber. More preferably, the island component resin has a melt viscosity of 800 at 240°C to 2000 poise.

Sea Component Resin

[0051] The sea component resin comprises a water-soluble or easily alkali-soluble thermoplastic resin (B). As the thermoplastic resin (B), there can be mentioned, for example, a thermoplastic resin capable of being dissolved in water (including heated water) and/or alkali. Preferred examples of the sea component resin may include a thermoplastic polyvinyl alcohol resin that is soluble to water and an easily-soluble polyester resin that is soluble to alkali.

[0052] For example, when immersed in hot water at 100°C at a bath ratio of 1:30, the thermoplastic polyvinyl alcohol resin can be dissolved (or disintegrated) substantially completely within a period of, for example, 60 minutes, preferably 50 minutes, more preferably 30 minutes, and especially preferably 15 minutes.

[0053] For example, when immersed in a 2% aqueous solution of sodium hydroxide at 100°C at a bath ratio of 1:30, the easily-soluble polyester resin can be dissolved (or disintegrated) substantially completely within a period of, for example, 60 minutes, preferably 45 minutes, more preferably 30 minutes, and especially preferably 15 minutes.

Thermoplastic Polyvinyl Alcohol Resin

[0054] A polyvinyl alcohol (which will hereinafter be referred to at times as a PVA) constituting the thermoplastic polyvinyl alcohol resin principally comprises a vinyl alcohol unit, may be a homopolymer of a vinyl alcohol unit, or a modified polymer including a vinyl alcohol unit copolymerized with a copolymerizable unit and/or including a vinyl alcohol unit and a functional group introduced thereto.

[0055] A PVA used in the present invention can be prepared from a vinyl ester-based polymer through saponification of vinyl ester units thereof. Examples of a vinyl compound monomer that forms such a vinyl ester unit may include vinyl formate, vinyl acetate, vinyl propionate, vinyl valerate, vinyl caprate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl pivalate, vinyl versatate, and others. Among them, vinyl acetate is preferred from the viewpoint of preparation of a PVA.

[0056] While a PVA used in the present invention may comprise a PVA homopolymer and/or a PVA polymer modified with a copolymerizable unit, it is preferred to use a polyvinyl alcohol which is modified with a copolymerizable unit, from the viewpoint of melt-spinnability, water-solubility, and physical properties of a fiber. Examples of copolymerizable monomers may include: α-olefins such as ethylene, propylene, 1-butene, isobutene, and 1-hexene; acrylic acids and salts thereof; acrylic esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, and i-propyl acrylate; methacrylic acids and salts thereof; methacrylic esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, and i-propyl methacrylate; acrylamides; acrylamide derivatives such as N-methyl acrylamide and N-ethyl acrylamide; methacrylamides; methacrylamide derivatives such as N-methyl methacrylamide and N-ethyl methacrylamide; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether, and n-butyl vinyl ether; hydroxy group-containing, vinyl ethers such as ethylene glycol vinyl ether, 1,3-propanediol vinyl ether, and 1,4-butanediol vinyl ether; allyl acetate; allyl ethers such as propyl allyl ether, butyl allyl ether, and hexyl allyl ether; oxyalkylene group-containing monomers; vinyl silyls such as vinyltrimethoxysilane; isopropenyl acetate; hydroxy group-containing α-olefins such as 3-buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, 7-octen-1-ol, 9-decen-1-ol, and 3-methyl-3-buten-1-ol; carboxyl group-containing monomers derived from, for example, fumaric acid, maleic acid, itaconic acid, maleic anhydride, phthalic anhydride, trimellitic anhydride, or itaconic anhydride; sulfonate group-containing monomers derived from, for example, ethylene sulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, or 2-acrylamide-2-methyl propane sulfonic acid; and cation group-containing monomers derived from, for example, vinyloxyethyltrimethyl ammonium chloride, vinyloxybutylt-

rimethyl ammonium chloride, vinyloxyethyldimethyl amine, vinyloxymethyldiethyl amine, N-acrylamidomethyltrimethyl ammonium chloride, N-acrylamidoethyltrimethyl ammonium chloride, N-acrylamidodimethyl amine, allyltrimethyl ammonium chloride, methallyltrimethyl ammonium chloride, dimethylallyl amine, or allylethyl amine.

[0057] Among these monomers, monomers derived from α-olefins such as ethylene, propylene, 1-butene, isobutene, and 1-hexene; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether, and n-butyl vinyl ether; hydroxy group-containing, vinyl ethers such as ethylene glycol vinyl ether, 1,3-propanediol vinyl ether, and 1,4-butanediol vinyl ether; allyl acetate; allyl ethers such as propyl allyl ether, butyl allyl ether, and hexyl allyl ether; oxyalkylene group-containing monomers; and hydroxy group-containing α-olefins such as 3-buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, 7-octen-1-ol, 9-decenl-ol, and 3-methyl-3-buten-1-ol are preferred for their accessibility and more. Particularly preferred are monomers derived from α-olefins and/or vinyl ethers.

[0058] Especially, α-olefins having 4 or less carbon atoms, including ethylene, propylene, 1-butene, and isobutene; and vinyl ethers with a linear or branched alkylene group bonded to a vinyl group and having 4 or less carbon atoms, such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether, and n-butyl vinyl ether are more preferred from the viewpoint of copolymerizability, melt-spinnability, and water-solubility of a fiber.

[0059] The monomer(s) may be typically present in the PVA at a content of 20% or less by mol, preferably 15% or less by mol, and more preferably 13% by mol or less. While no specific lower limit is given for the content of the monomer(s), a content of, for example, 0.1% or more by mol, preferably 3% or more by mol, and more preferably 6% or more by mol may be used as the lower limit.

[0060] Specifically, it is preferred that the modified PVA polymer used include from 4 to 15% by mol, and more preferably from 6 to 13% by mol of an ethylene unit when ethylene is used as a modifying α-olefin, for better physical properties of a fiber.

[0061] A PVA used in the present invention preferably has a viscosity-average polymerization degree (which will hereinafter be referred to in short as a polymerization degree) of from 200 to 500, more preferably from 230 to 470, and especially preferably from 250 to 450, from the viewpoint of spinnability and solubility. In particular, the use of a so-called low polymerization degree PVA having a polymerization degree of 500 or less can not only increase the speed of dissolution of the sea component in the sea-island type composite multifilament in an aqueous solution but can also minimize shrinkage of the sea-island type composite multifilament during the dissolution.

[0062] The polymerization degree (P) of the PVA is determined on the basis of JIS K 6726. That is, the PVA is re-saponified and purified to subsequently measure the limiting viscosity number [η] (in dL/g) of the resultant in water at 30°C, from which the polymerization degree (P) of the PVA is determined according to the following equation:

$$P = ([\eta] \times 10^3/8.29)^{(1/0.62)}$$

[0063] A PVA used in the present invention may preferably have a saponification degree of from 90 to 99.99% by mol, from the viewpoint of spinnability and solubility. More preferably, the degree of saponification of the PVA is from 93 to 99.98% by mol, further preferably from 94 to 99.97% by mol, and especially preferably from 96 to 99.96% by mol.

[0064] In particular, PVA used in the present invention may preferably have a mole fraction of a central hydroxyl group in a triad of hydroxyl groups on triad display relative to vinyl alcohol units in the PVA of from 70 to 99.9% by mol, more preferably from 72 to 99% by mol, further preferably from 74 to 97% by mol, and especially preferably from 76 to 95% by mol.

[0065] In the context of the present invention, it should be noted that a central hydroxyl group in a triad of hydroxyl groups on triad display in a polyvinyl alcohol means a peak (I) representing the tacticity of triads of hydroxyl group protons as measured at 500 MHz and 65°C in a d6-DMSO solution of the PVA by means of a proton NMR spectrometer GX-500 (available from JEOL, Ltd.). The peak (I) is defined by the total contribution from isotactic triads (at 4.54 ppm), heterotactic triads (at 4.36 ppm), and syndiotactic triads (at 4.13 ppm) on triad display of hydroxyl groups in a PVA, while the peak (II) for each hydroxyl group on all of the vinyl alcohol units of the PVA appears in the chemical shift range from 4.05 ppm to 4.70 ppm. Therefore, the mole fraction of a central hydroxyl group in a triad of hydroxyl groups on triad display relative to vinyl alcohol units in a PVA according to the present invention can be expressed as 100 x peak (I) / peak (II).

[0066] Further, where a PVA according to the present invention comprises an ethylene-modified PVA, the effect of the present invention can be further enhanced where the following formula is satisfied:

$$-1.5 \times Et + 100 \geq \text{Mole Fraction} \geq -Et + 85$$

[0067] In the above formula, Mole Fraction (in % by mol) represents the mole fraction of a central hydroxyl group in a triad of hydroxyl groups on triad display relative to vinyl alcohol units of a PVA, and Et represents the content of ethylene

moiety (in % by mol) in the vinyl alcohol-based polymer.

[0068] A PVA used in the present invention preferably has a melting point (Tm) of 160 to 230°C, more preferably 170 to 227°C, further preferably 175 to 224°C, and especially preferably 180 to 220°C. It should be noted that a melting point of a PVA means a temperature of a peak top of an endothermic peak obtained using DSC under nitrogen atmosphere by elevating temperature into 250°C at an elevating rate of 10°C/min, cooling down to a room temperature, and then reelevating temperature into 250°C at an elevating rate of 10°C/min to obtain the peak top of the endothermic peak.

[0069] A PVA used in the present invention preferably comprises an alkali metal ion from the viewpoint of improvement in solubility. The PVA preferably has a proportion of content of sodium ion equivalent to the alkali metal ion(s) of from 0.0003 to 1 part by mass, more preferably from 0.0003 to 0.8 parts by mass, further preferably from 0.0005 to 0.6 parts by mass, and especially preferably from 0.0005 to 0.5 parts by mass relative to 100 parts by mass of the PVA. Examples of the alkali metal ion include a potassium ion and a sodium ion.

[0070] While any method can be used according to the present invention to incorporate a predetermined amount of the alkali metal ion(s) into the PVA. There may be mentioned a method adding a compound(s) containing an alkali metal ion(s) to a polymerized PVA, and a method incorporating alkali metal ion(s) into a PVA by using an alkaline substance(s) containing the alkali ion(s) as a saponification catalyst upon saponifying a vinyl ester polymer in a solvent, and washing the resultant saponified PVA with a washing liquid so as to control a content of the alkali metal ion(s) present in the PVA. Among them, the latter method is preferred. It should be noted that the content of the alkali metal ion(s) in the PVA can be determined by means of atomic absorption spectroscopy.

[0071] Further, the thermoplastic polyvinyl alcohol resin may comprise from 1 to 30% by mass, and preferably from 2 to 20% by mass of a plasticizer, as necessary, relative to the mass of the PVA for the purpose of improving the melt fluidity at an elevated temperature and spinnability of the PVA. Examples of the plasticizer may include a polyethylene glycol, propylene glycol and an oligomer thereof, butylene glycol and an oligomer thereof, a polyglycerin derivative, a glycerin derivative in the form of an adduct of an alkylene oxide such as an ethylene oxide or a propylene oxide, a sorbitol derivative in the form of an adduct of an alkylene oxide such as an ethylene oxide or a propylene oxide, a polyol such as pentaerythritol and a derivative thereof, and a PO/EO random copolymer.

[0072] In particular, for the purpose of achieving advantageous plasticizability and spinnability with less inclination to thermal decomposition during a filament forming process, a plasticizer such as an alkylene oxide adduct of sorbitol, a monoester of poly glycerin and alkyl carboxylic acid, and/or a PO/EO random copolymer is preferably incorporated to the thermoplastic polyvinyl alcohol resin at a proportion of from 1 to 30% by mass, and preferably from 2 to 20% by mass. Especially preferred is a compound of sorbitol in the form of an adduct of from 1 to 30 moles of an ethylene oxide.

Easily-soluble Polyester Resin

[0073] Examples of the easily-soluble polyester resin may include a polar group-containing copolyester and an aliphatic polyester.

[0074] For example, as the polar group-containing copolyester, there can be mentioned a copolyester comprising a dicarboxylic acid unit, such as terephthalic acid and isophthalic acid, and a diol unit, such as ethylene glycol, that are copolymerized with an ester-forming compound of metal sulfonate (e.g., sodium 4-sulfoisophthalate, potassium 5-sulfoisophthalate, sodium 5-sulfoisophthalate, sodium 4-sulfoterephthalate, potassium 5-sulfoterephthalate, and sodium 4-sulfophthalate).

[0075] It should be noted that, aside from terephthalic acid and isophthalic acid, examples of the dicarboxylic acid unit may include: aromatic dicarboxylic acids such as diphenyl sulfone dicarboxylic acid, benzophenone dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid, and 3,3'-diphenyl dicarboxylic acid; aliphatic dicarboxylic acids such as adipic acid, succinic acid, azelaic acid, sebacic acid, and dodecanedioic acid; and alicyclic dicarboxylic acids such as hexahydroterephthalic acid and 1,3-adamantane dicarboxylic acid.

[0076] Aside from ethylene glycol, examples of the diol unit may include: aromatic diols such as chlorohydroquinone, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenylsulfide, 4,4'-dihydroxybenzophenone, and p-xyleneglycol; aliphatic diols such as diethylene glycol, propanediol, butanediol, hexanediol, and neopentylglycol; and alicyclic diols such as cyclohexanedimethanol.

[0077] For example, 1 to 20% by mol, preferably 1 to 12% by mol, and more preferably 1 to 5% by mol of the ester-forming metal salt compound of sulfonic acid may be used relative to the total mole of dicarboxylic acid components of the polar group-containing copolyester considering the balance between easy solubility to water and water resistance.

[0078] Furthermore, a polyalkylene glycol (e.g., a poly(C_{1-4} alkylene glycol) such as a polypropylene glycol and a polyethylene glycol) may be copolymerized, and may be incorporated at a concentration of, for example, about from 5 to 30% by mass, and preferably about from 6 to 25% by mass in the polar group-containing copolyester.

[0079] Meanwhile, examples of the aliphatic polyester include a polylactic acid; polyesters of an aliphatic diol and an aliphatic carboxylic acid such as a polyethylene succinate), a poly(butylene succinate), and a poly(butylene succinate-co-butylene adipate); polyhydroxycarboxylic acids such as a poly(glycolic acid), a poly(3-hydroxybutyric acid), a poly(3-

hydroxyvaleric acid), and a poly(6-hydroxycaproic acid); and poly(ω-hydroxyalkanoates) such as a poly(ε-caprolactone) and a poly(δ-valerolactone). These aliphatic polyesters can be used alone, or combination of two or more. Preferred among them is a polylactic acid which may comprise a poly(D-lactic acid), a poly(L-lactic acid), or a mixture thereof.

[0080] The sea component resin preferably has a melt viscosity at 240°C of 600 to 3000 poises from the viewpoint of better filament-forming property. There is a possibility that a melt viscosity of more than 3000 poise of the sea component resin may result in poor, high-speed spinnability during filament-forming process. Meanwhile, a melt viscosity of less than 600 poise of the sea component resin may result in poor productivity due to an increased chance of a filament breakage during spinning process and may also result in a low tenacity of the obtained fiber. More preferably, the sea component resin has a melt viscosity at 240°C of from 800 to 2000 poise.

Production Process of Sea-island type Composite Multifilament

[0081] The sea-island type composite multifilament according to the present invention can be produced by means of a traditionally known conjugate spinning system. Even though a thermoplastic elastomer resin is used as an island component thereof, the island component can be formed into a shape of ultrafine filaments by using a thermoplastic elastomer resin (A) having a hardness in a specific range as the island component, by lowering the single filament fineness of the sea-island type composite multifilament, and by decreasing the number of islands of the island component in the sea-island type composite multifilament at the same time.

[0082] The process for producing the sea-island type composite multifilament comprises melt-kneading an island component resin and a sea component resin in respective extruders to provide resin melts separately, discharging the resin melts of the island component resin and the sea component resin at a predetermined composite ratio between the island component and the sea component from a conjugate spinning nozzle to which the resin melts are introduced to give discharged filaments(or as-spun melt filaments), and winding the discharged filaments at a predetermined take-up speed (or spinning speed).

[0083] At the melt-kneading step, the island component resin and the sea component resin are each melted at a temperature depending on the melting point of each of the resins. If necessary, an additive(s) such as the color enhancer and the plasticizer may be mixed in during the melt-kneading. The additive(s) may be added directly or, alternatively, may be first prepared in the form of a master batch and further kneaded together with the island component resin and/or the sea component resin.

[0084] At the discharging step, it is preferred that the number of islands per filament be low. For example, the number of islands per filament may be from 3 to 200. Preferably, the number of islands per filament may be from 5 to 100, more preferably from 6 to 80, and further preferably from 7 to 60, in view of high-speed spinnability and filament production stability. Where the number of islands per filament is higher than the stated upper limit, there is a possibility that high stretchability of a thermoplastic elastomer may cause adhesion of islands with each other due to shrinkage of the island components from the period of conjugatespinning of the island component resin and the sea component resin to the period of cool-solidification of the resultant.

[0085] Preferably, the composite ratio between the sea component and the island component in terms of a mass ratio (sea: island) is from 20:80 to 70:30, more preferably from 25:75 to 70:30, and further preferably from 30:70 to 60:40 in view of high-speed spinnability and grip performance.

[0086] Preferably, the discharged filament is subjected to direct drawing (or spin-drawing) instead of being wound in an as-spun form. For example, right after the filament is discharged (or after, in turn, being subjected to a cooling step as necessary), the filament may be subjected to a direct drawing step and successively wound as a drawn filament.

[0087] At the cooling step, the discharged filament may be cooled in a quenching zone. For example, in the quenching zone, the discharged filament can be cooled and solidified with the use of cooling air. Further, at the direct drawing step, the cooled and solidified filament may be drawn.

[0088] At the winding step, the filament may be taken up at a take-up speed of, for example, from 2000 to 4000 m/min. In view of filament production stability, the take-up speed may preferably be from 2200 to 3800 m/min, and more preferably from 2300 to 3700 m/min.

[0089] A sea-island type composite multifilament according to the present invention exhibits advantageous spinnability, because an island component resin comprising the thermoplastic elastomer resin is enclosed in a sea component resin comprising a non-thermoplastic elastomer resin in the sea-island type composite multifilament. Furthermore, the sea-island type composite multifilament after the winding step shows advantageous unwindability during a rewinding process.

[0090] The sea-island type composite multifilament may have a single filament fineness of, for example, from 0.5 to 5 dtex, preferably from 0.8 to 4.5 dtex, and more preferably from 1 to 4 dtex. The single filament fineness in this context is determined in accordance with a procedure described in the Examples section below. Where the single filament fineness is greater than the stated upper limit, it may result in deteriorated handleability, such as deteriorated physical properties of a fiber and deteriorated unwindability, due to delayed cooling and solidification of the fiber and the accompanying separation between the island component and the sea component.

[0091] The sea-island type composite multifilament can have a small average single island fineness. For example, the sea-island type composite multifilament may have an average single island fineness of from 0.005 to 0.5 dtex, preferably from 0.010 to 0.4 dtex, and more preferably from 0.015 to 0.3 dtex. The average single island fineness in this context is determined in accordance with a procedure described in the Examples section below.

[0092] The sea-island type composite multifilament may have a fiber strength at a room temperature of, for example, 1.0 cN/dtex or more, and preferably 1.1 cN/dtex or more from the viewpoint of processibility. While no specific upper limit is given for the fiber strength, a fiber strength at a room temperature of, for example, 2.5 cN/dtex or less may be used as the upper limit, since an island component resin of the sea-island type composite multifilament comprises a thermoplastic elastomer resin. The fiber strength in this context is determined in accordance with a procedure described in the Examples section below.

[0093] The produced sea-island type composite multifilament may be used in the original form as a continuous filament or, alternatively, be processed by being cut to staples, etc. Further, the produced sea-island type composite multifilament may be interknitted, interwoven, or admixed with one or more additional natural and/or synthetic fibers for use.

Fiber Structure Comprising Sea-island type Composite Multi filament

[0094] One embodiment of the present invention encompasses a fiber structure comprising, at least in part thereof, the sea-island type composite multifilament and/or a cut fiber thereof. As the fiber structure, there may be mentioned: a one-dimensional structure such as a yarn product, a string product, and a rope product, each constituted by a spun yarn comprising the sea-island type composite multifilament and/or a cut fiber thereof; a two-dimensional structure such as woven and/or knitted fabric(s), each comprising the sea-island type composite multifilaments and/or spun yarns comprising cut fibers thereof, and a nonwoven fabric comprising cut fibers of the sea-island type composite multifilament; and a three-dimensional structure comprising one or more of such structures. The fiber structure may comprise the sea-island type composite multifilament as a sole fiber or may, alternatively, comprise one or more additional fibers chosen from a natural fiber, a man-made fiber, a synthetic fiber, and others, in addition to the sea-island type composite multifilament(s).

Ultrafine Multifilament and Ultrafine Fiber Structure

[0095] According to the present invention, in an aspect thereof, an ultrafine multifilament can be produced in a process for producing an ultrafine multifilament, which comprises at least a step of dissolving the thermoplastic resin (B) to be removed from the aforementioned sea-island type composite multifilament. Alternatively, an ultrafine fiber structure can be produced in a process for producing an ultrafine fiber structure, which comprises at least dissolving the thermoplastic resin (B) to be removed from a fiber structure comprising, at least in part thereof, the sea-island type composite multifilament and/or a cut fiber thereof.

[0096] The removal of the sea component comprising the thermoplastic resin (B) may be carried out by removing the sea component through a treatment, such as an alkali treatment or an aqueous treatment, selected depending on the type of a resin constituting the sea component. The aqueous treatment may involve the use of water and/or an aqueous solution, while the alkali treatment may involve the use of an aqueous alkali solution, etc.

[0097] The dissolving for removal step may be performed at a temperature of, for example, from 50 to 120°C, and preferably from 80 to 100°C, depending on the type of a treatment solution used therefor, etc.

[0098] The ultrafine multifilament comprises a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less and may have a coefficient of fiber-to-metal dynamic friction of 0.30 or more. Preferably, the coefficient of fiber-to-metal dynamic friction of the ultrafine multifilament may be 0.33 or more, and more preferably 0.36 or more. , While no specific upper limit is given for the coefficient of fiber-to-metal dynamic friction, the upper limit of the coefficient of fiber-to-metal dynamic friction may be, for example, 1.0 or less, and preferably 0.50 or less. The coefficient of fiber-to-metal dynamic friction is determined in accordance with a procedure described in the Examples section below.

[0099] The ultrafine multifilament may have a single filament fineness of, for example, from 0.005 to 0.5 dtex, preferably from 0.01 to 0.4 dtex, and more preferably from 0.015 to 0.3 dtex. The single filament fineness in this context is determined in accordance with a procedure described in the Examples section below. By having a small single filament fineness, the ultrafine multifilament can have a higher coefficient of friction, thereby achieving improved grip performance.

[0100] The ultrafine multifilament may have a fiber tenacity at a room temperature of, for example, 1.0 cN/dtex or more, preferably 1.1 cN/dtex or more, and more preferably 1.2 cN/dtex or more. While no specific upper limit is given for the fiber strength, a fiber tenacity at a room temperature of, for example, 2.5 cN/dtex or less may be used as the upper limit, since the ultrafine multifilament comprises a thermoplastic elastomer resin. The fiber tenacity in this context is determined in accordance with a procedure described in the Examples section below.

[0101] One embodiment of the present invention encompasses an ultrafine fiber structure comprising, at least in part

thereof, the ultrafine multifilament and/or a cut fiber of the ultrafine multifilament. It should be noted that the ultrafine multifilament and/or a cut fiber of the ultrafine multifilament herein will sometimes be referred to, collectively and in short, as an ultrafine fiber. An ultrafine multifilament and an ultrafine fiber aggregate according to the present invention can exhibit advantageous grip performance due to a friction force which is, perhaps, attributed to frictions between the single filaments of the ultrafine fiber originating from the ultrafine multifilament.

[0102] Examples of the ultrafine fiber structure may include a thread-form product of the ultrafine multifilament(s) and cut fibers thereof, and a woven and/or knitted fabric of the ultrafine multifilaments and cut fibers thereof, as well as a nonwoven fabric comprising cut fibers of the ultrafine multifilament. The ultrafine fiber structure may comprise the ultrafine fiber(s) as a sole fiber or may, alternatively, comprise one or more additional fiber(s) chosen from a natural fiber(s), a man-made fiber(s), a synthetic fiber(s), and others, together with the ultrafine fiber(s).

[0103] As the ultrafine fiber structure, there can be mentioned: a one-dimensional structure such as a yarn product, a string product, and a rope product, each constituted by the ultrafine multifilament and/or a cut fiber thereof; a two-dimensional structure such as woven and/or knitted fabric(s), each comprising the ultrafine multifilaments and/or spun yarns comprising cut fibers thereof and a nonwoven fabric comprising cut fibers of the ultrafine multifilament; and a three-dimensional structure comprising one or more of such structures. The fiber structure may comprise the ultrafine multifilament as a sole fiber or may, alternatively, comprise one or more additional fibers chosen from a natural fiber, a man-made fiber, a synthetic fiber, and others, in addition to the ultrafine multifilament(s).

[0104] For example, the ultrafine fiber structure may comprise from 20 to 100% by mass, preferably from 30 to 100% by mass, and further preferably from 40 to 100% by mass of the ultrafine multifilament and/or a cut fiber thereof.

[0105] Moreover, the ultrafine multifilament and/or a cut fiber thereof as well as the ultrafine fiber structure may be dyed, since an ultrafine multifilament and/or a cut fiber thereof according to the present invention exhibit(s) excellent color development performance. A dyeing step therefor can be carried out by means of a conventional method chosen depending on a dyeing agent to be used.

[0106] Examples of the dyeing agent may include an acid dye, an acid mordant dye, a metal complex acid dye, and a disperse dye. Among them, an acid dye, an acid mordant dye, and a metal complex acid dye are preferred from the viewpoint of color development performance and spinnability.

[0107] The acid dye is a dye containing a soluble group such as a sulfonate group, a carboxyl group, and a hydroxy group. Examples of the acid dye may include an azo-based dye, a triphenylmethane-based dye, an anthraquinone-based dye, an oxo-anthracene-based dye, a phthalocyanine-based dye, an Indigoid-based dye, a nitroso group-based dye, and a pyrazolone-based acid dye.

[0108] The acid mordant dye is a dye that forms, for the large part, a metal complex (e.g., a coordinate bond with a chromium atom) while at the same time exhibiting color development performance based on the mechanism of an acid dye. Examples of the acid mordant dye may include an azo-based dye, a triphenylmethane-based dye, an anthraquinone-based dye, an oxo-anthracene-based dye, a phthalocyanine-based dye, an Indigoid-based dye, a nitroso group-based dye, and a pyrazolone-based acid mordant dye.

[0109] The metal complex acid dye can be largely classified into a 1:1 type dye in which one metal atom is coordinated with one dye molecule and a 1:2 type dye in which one metal atom is coordinated with two dye molecules. Examples of the metal complex acid dye may include an azo-based dye, a triphenylmethane-based dye, an anthraquinone-based dye, an oxo-anthracene-based dye, a phthalocyanine-based dye, an Indigoid-based dye, a nitroso group-based dye, and a pyrazolone-based metal complex acid dye.

[0110] An ultrafine multifilament according to the present invention may exhibit excellent color development performance and, in particular, exhibits excellent color development performance in deep color dyeing with navy blue color, dark brown color, black color, etc. For example, an ultrafine multifilament according to the present invention may exhibit an L* value of 70 or less, preferably 60 or less, more preferably 50 or less, and further preferably 45 or less, as measured after deep color dyeing. A lower L* value means greater color deepness. While no specific lower limit is given for the L* value, an L* value of, for example, 10 or more may be used as the lower limit. It should be noted that an L* value is determined in accordance with a procedure described in the Examples section below.

[0111] Furthermore, an ultrafine fiber structure according to the present invention exhibits superior color fastness to washing and, for example, ranks as grade 4 or greater when assessed in accordance with the test method for color fastness to washing that is stipulated in JIS L 0844.

EXAMPLES

[0112] Hereinafter, the present invention will be demonstrated by way of some examples that are presented only for the sake of illustration, which are not to be construed as limiting the scope of the present invention.

Hardness

Shore A Hardness

[0113] In accordance with JIS K 7215, a durometer hardness (Shore A hardness) of an island component resin was measured by means of a durometer using a type A indenter (having a frustoconical tip, a tip diameter of 0.79 mm, and a cone angle of 35°).

Shore D Hardness

[0114] In accordance with JIS K 7215, a durometer hardness (Shore D hardness) of an island component resin was measured by means of a durometer using a type D indenter (having a conical tip, a tip diameter of 0.1 mm, and a cone angle of 30°).

Rockwell hardness (R scale)

[0115] In accordance with JIS Z 2245, a Rockwell hardness (R scale) of an island component resin was measured using a rigid ball having a diameter of 12.7 mm as an indenter.

Average Single Island Diameter

[0116] An average single island diameter was measured in the following procedure: each of the sea-island type composite multifilaments prepared in the Examples and Comparative Examples was used to prepare a cylindrical knitted fabric. The cylindrical knitted fabric was treated in hot water at 95°C at a bath ratio of 1:30 for 20 minutes to dissolve a sea component to be removed therefrom, followed by the drying of the resultant. Then, a cross-sectional view of filaments was observed using a scanning electron microscope JCM-6000Plus (available from JEOL, Ltd.) to measure diameters of 10 filaments randomly selected in the micrograph of the cross-sectional view. An average value of these measurements was calculated and used as an average single island diameter.

Fineness

[0117] A fineness was measured on the basis of JIS L 1013 "Testing methods for man-made filament yarns." A total fineness refers to the fineness of a multifilament as a whole, while a single filament fineness refers to a value obtained by dividing the total fineness by the number of filaments.

Spinnability

[0118] The occurrence of a filament breakage in a sea-island type composite multifilament when spun at a rate of 3000 m/min was assessed by means of the following evaluations:

A: No filament breakage occurred for 24 hours or longer;
B: Filament breakage occurred in from 3 hours to shorter than 24 hours;
C: Filament breakage occurred in from more than 1 hour to less than 3 hours; and
D: Filament breakage occurred within no more than 1 hour.

Unwindability

[0119] A spun and wound, sea-island type composite multifilament was rewound at a speed of 200 m/min for 300 minutes to assess the occurrence of a filament breakage as well as fluffs and loops in the sea-island type composite multifilament using the following evaluations:

A: No filament breakage occurred with no fluffs or loops;
B: No filament breakage occurred, but fluffs and/or loops found; and
C: Filament breakage occurred.

Fiber tenacity

[0120] In accordance with JIS L 1013, fiber tenacity and elongation at break (or an initial tensile resistance) were

determined under the conditions including a sample length of 20 cm, an initial load of 0.1 g/d, and a tension rate of 10 cm/min. An average value of the measurements at 5 or more different points was used as a fiber tenacity.

Coefficient of Fiber-to-metal Dynamic Friction

[0121] Each of the sea-island type composite multifilaments prepared in the Examples and Comparative Examples was treated by dissolving the sea component to be removed therefrom. Then, a fiber-to-metal travel friction tester comprising a frictional body in the form of an aventurine chrome plated pin with a diameter of 60 mm was used to measure a tension force (T2) on the side of fed-out frictional body under the conditions of a tension force (T1) of 10 g on the side of fed-in frictional body, a travel speed of 300 m/min, and a contact angle of 180°. The coefficient (t) of fiber-to-metal dynamic friction of the sample was calculated from the well-known following equation concerning the friction of a belt that travels on a cylinder:

$$f = (1/\pi) \times \ln(T2/T1)$$

L* Value

[0122] A circular knitting machine (in 18 gauge) was used to prepare a circular knitted fabric from each of the ultrafine multifilaments prepared in the Examples and Comparative Examples. The L* value of the fabric was determined using a spectrophotometer "CM-3700A" available from KONICA MINOLTA, INC. under the conditions including a specular reflectance setting: SCE, a measurement area diameter: LAV (with 25.4 mm), UV condition setting: 100%Full, a viewing angle: 2°, and a main light source: D65 light source.

Dyeing Conditions

[0123] It should be noted that a circular knitting machine (in 18 gauge) was used to prepare a circular knitted fabric from each of the prepared sea-island type composite multifilaments. Then, the resulting sample was treated in hot water at 100°C at a bath ratio of 1:30 for 40 minutes to dissolve a sea component to be removed therefrom to prepare a circular knitted fabric comprising ultrafine multifilaments. It should be noted that the circular knitted fabric originating from each of Examples 1 to 7 and Comparative Examples 3 to 5 was dyed with an acid dye, while the circular knitted fabric originating from each of Example 8 and Comparative Examples 1 and 2 was dyed with a disperse dye. The assessments on the L* values of these circular knitted fabrics are shown in Table 1.

Dyeing Method for Acid Dye

Dyeing Conditions

[0124]

Dye: 4%owf Kayanol Milling Black TLB (available from NIPPON KAYAKU Co., Ltd.)
Dyeing Aids: 2.0%owf UNIGAL ASS-10 (available from Meisei Chemical Works, Ltd.), 0.5 g/L ammonium sulfate (available from NIPPON KAYAKU Co., Ltd.), and 2%owf acetic acid
Bath Ratio: 1/50
Dyeing Temperature x Duration: 90°C for 40 minutes

Soaping

[0125]

1 g/L LACCOL PSK (available from Meisei Chemical Works, Ltd.)
Bath Ratio: 1/50
Dyeing Temperature x Duration: 70°C for 40 minutes

Dyeing Method for Disperse Dye

Dyeing Conditions

[0126]

Dye: 4.0%owf Kayalon Polyester Black ECXN300
Dyeing Aids: 1.0 cc/L Disper TL and 1.0 cc/L acetic acid
Bath Ratio: 1/50
Dyeing Temperature x Duration: 120°C for 40 minutes

Reduction Cleaning

[0127]

1.0 g/L sodium hydroxide, 1.0 g/L sodium hydrosulfite, and 1.0 g/L Amiradine D
Bath Ratio: 1/50
Reduction Cleaning Temperature x Duration: 70°C for 20 minutes

Color Fastness to Washing

[0128] A circular knitting machine (in 18 gauge) was used to prepare a circular knitted fabric from each of the fibers prepared in the Examples and Comparative Examples. The prepared circular knitted fabrics were dyed in the same manner as those used in the L* value measurement. Then, the color fastness to washing of each circular knitted fabric was determined in accordance with a measurement procedure stipulated in JIS L 0844 B-4.

Grip Performance Assessment

[0129] A circular knitting machine (in 18 gauge) was used to prepare a circular knitted fabric from each of the sea-island type composite multi filaments prepared in the Examples and Comparative Examples. The prepared circular knitted fabric was immersed in hot water at 90°C for 30 minutes and was, then, passed through a tunnel-type setter at 160°C in 1 minute to prepare a circular knitted fabric formed with ultrafine multifilaments.

[0130] The resulting circular knitted fabric was processed into a fabric piece having a size of 10 cm (width) x 50 cm (length). The fabric piece was wound in three turns around an assessor's arm, and a 200 g load was applied to the remaining free end of the fabric piece. After three minutes, the assessor evaluated the feeling of slippage of the fabric piece. Such a sensory evaluation was made by 10 assessors in accordance with the following evaluation score criteria:

2 scores if no slippage is felt;
1 score if a slight level of slippage is felt; and
0 score if slippage is definitely felt.

[0131] Then, a total score of the assessors' evaluations was calculated and used to draw a conclusion on grip performance based on the following ranks:

Rank A if the total score is 15 or higher;
Rank B if the total score is from 11 to 14;
Rank C if the total score is from 7 to 10; and
Rank D if the total score is 6 or less.

Coefficient of Dynamic Friction (for Fabric)

[0132] In accordance with ASTM D 1894, a coefficient of dynamic friction for a fabric was measured using Instron 5500R (model 2810-005 available from Instron) with a coefficient-of-friction test jig.

[0133] Bioskin (available from Beaulax Co., Ltd.) was affixed to a horizontal table of the jig with a double-sided tape. For a test sample, a circular knitted fabric formed from ultrafine multifilaments and prepared in the same way as in the grip performance assessment was affixed to a 200-g movable sled with a double-sided tape. Then, a measurement was made at a traveling speed of 100 mm/min over a measurement distance of 150 mm.

[0134] A single measurement was carried out by using one sample. The average value of five measurements was

used as a coefficient of dynamic friction with the third decimal place rounded off to the second decimal place .

Example 1

[0135] A polyamide-based elastomer, nylon(Ny) 12 elastomer-1 (E1.-1) "VESTAMID E47-S1" (available from Daicel-Evonik) as an island component resin and an ethylene-modified polyvinyl alcohol copolymer (with a saponification degree of 98.5 mol%, an ethylene content of 8.0 mol%, and a polymerization degree of 380) (available from KURARAY CO., LTD.) as a sea component resin were used at a composite ratio between the island component and the sea component of 50/50 (in mass ratio). These components were each melted in a separate extruder, and were discharged from a conjugate spinning nozzle to obtain as-spun filaments having 37 islands per mono filament.

[0136] Next, the as-spun filaments discharged from the spinneret was quenched using a horizontal air flow cooling system spanning a length of 1.0 m. Then, the filaments were successively introduced into a tube heater disposed at a location 1.3 m directly below the spinneret spanning a length of 1.0 m and having an inner diameter of 30 mm (at an inner wall temperature of 180°C) so as to subject the quenched filaments for direct drawing in the tube heater. Subsequently, a finishing oil was applied to the filaments from the tube heater. The filaments were successively wound through a roller at a take-up speed of 3000 m/min to provide a sea-island type composite multifilament having 84 dtex and 24 filaments.

[0137] The resulting sea-island type composite multifilament was treated in hot water at 100°C at a bath ratio of 1:30 for 40 minutes to dissolve the sea component to be removed therefrom to prepare an ultrafine multifilament comprising a thermoplastic elastomer resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 2

[0138] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that the number of islands per monofilament of the sea-island type composite multifilament was 12. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 3

[0139] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that the number of islands per monofilament of the sea-island type composite multifilament was 7 and the composite ratio of a sea component to an island component was 30/70 in mass ratio. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 4

[0140] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that the filament number of the sea-island type composite multifilament was 72. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 5

[0141] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that the number of islands per monofilament of the sea-island type composite multifilament was 100. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 6

[0142] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a polyamide-based elastomer, Ny 12 elastomer-2 "VESTAMID E55-S4" (available from Daicel-Evonik) was used as an island component resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 7

(1) Preparation of Polyamide 12 Oligomer

[0143] Lauryl lactam (1000 g) and dodecanediamine (38 g) were introduced together with small amounts of water and phosphoric acid into an autoclave purged with nitrogen. The resulting mixture was agitated under heat. While implementing pressure control using nitrogen gas to maintain a pressure of 17.5 kgf/cm^2 (i.e., 1.7 $\times$ 10^6 Pa), the temperature of the reaction system was gradually elevated up to 270°C at which the agitation under heat was continued for about 4 hours. Next, the pressure of the reaction system was gradually lowered down to an ambient pressure. Then, while a very small amount of nitrogen gas was in circulation, the pressure was further lowered for about 1 hour to remove moisture and water content in the system. Subsequently, the system was cooled at an ambient pressure to extract a polyamide 12 oligomer in a melted form. The extracted polyamide 12 oligomer was further cooled to obtain a somewhat brittle solid of the polyamide 12 oligomer. The polyamide 12 oligomer had a relatively low, number-average molecular weight of about 5400, with an amino end group content of 350 μeq/g. This polyamide 12 oligomer was used as an amino group-containing color enhancer.

[0144] (2) A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that the polyamide 12 oligomer prepared in the above-mentioned manner was added to the island component resin at a proportion of 9% by weight. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Example 8

[0145] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a polyester-based elastomer, PET elastomer "HYTREL4047N" (available from DU PONT-TORAY CO., LTD.) was used as an island component resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multi filament.

Comparative Example 1

[0146] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a generic polyethylene terephthalate (PET) was used as an island component resin and the number of islands per monofilament of the sea-island type composite multifilament was 726. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Comparative Example 2

[0147] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a generic polyethylene terephthalate (PET) was used as an island component resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Comparative Example 3

[0148] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a polyamide-based elastomer, Ny 12 elastomer-3 "VESTAMID E62-S1" (available from Daicel-Evonik) was used as an island component resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Comparative Example 4

[0149] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a nylon(Ny) 6 "1013B" (available from Ube Industries, Ltd.) was used as an island component resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Comparative Example 5

[0150] A sea-island type composite multifilament and an ultrafine multifilament comprising a thermoplastic elastomer resin were spun and prepared in the same way as those of Example 1, except that a polyamide-based elastomer, Ny 11 elastomer "PEBAX Rnew 70R53" (available from ARKEMA) was used as an island component resin. Table 1 shows the evaluations of the prepared sea-island type composite multifilament and ultrafine multifilament.

Table 1

		Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Com. Ex_ 1	Com. Ex.2	Com. Ex.3	Com. Ex.4	Com. Ex.5
Sea-Island Type Composite Multifilament														
Island Component Resin Species		Ny 12 El.-1	Ny 12 El.-1	Ny 12 El-1	Ny 12 El.-1	Ny 12 El.-1	Ny 12 El-2	Ny 12 El.-1	PET El.	I PET	PET	Ny 12 El.-3	6	' Ny 11 El.
Hardness	Shore A (Durometer)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	90	N/A	N/A	N/A	N/A	N/A
	Shore D (Durometer)	47	47	47	47	47	55	47	40	N/A	N/A	62	N/A	70
	Rockwell (R Scale)	58	58	58	58	58	60	58	<50	125	125	72	120	80
Avg. Single Island Diameter (mm)		2200	3690	5640	1200	1280	2200	2200	2200	426	2200	2200	2200	2200
Single Island Fineness (dtex)		0.047	0.15	0.35	0.016	0.018	0.047	0.047	0.047	0.002	0.047	0.047	0.047	0.047
Island No.		37	12	7	37	100	37	37	37	726	37	37	37	37
Sea Component Resin Species		PVA	PVA	PVA	PVA	PVA	PVA	PVA	PVA	PVA	PVA	PVA	PVA	PVA
Sea /Island (wt%)		50/50	50/50	30/70	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50
Total Fineness (dtex)		84	84	84	84	84	84	84	84	84	84	84	84	84
Filament No.		24	24	24	72	24	24	24	24	24	24	24	24	I 24
Single Filament Fineness (dtex)		3.50	3.50	3.50	1.17	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Spinnability		A	A	A	A	B	A	A	A	D	A	B	A	B
Unwindability		A	A	A	A	A	A	A	A	C	A	A	A	A
Fiber tenacity (cN/dtex)		1.71	1.86	1.92	1.68	1.39	1.79	1.31	1.74	2.13	2.31	1.57	2.09	1.57
Ultrafine Multifilament														

(continued)

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Com. Ex_1	Com. Ex.2	Com. Ex.3	Com. Ex.4	Com. Ex.5
Total Fineness (dtex)	42	42	59	42	42	42	42	42	42	42	42	42	42
Filament No.	888	288	168	2664	2400	888	888	888	17424	888	888	888	888
Single Filament Fineness (dtex)	0.047	0.150	0.350	0.016	0.018	0.047	0.047	0.047	0.002	0.047	0.047	0.047	0.047
Fiber tenacity (cN/dtex)	1.68	1.85	1.91	1.57	1.21	1.77	1.29	1.71	2.07	2.29	1.51	1.99	1.51
Coefficient of Fiber-to-metal Dynamic Friction	0.37	0.35	0.32	0.40	0.39	0.34	0.34	0.36	0.29	0.17	0.26	0.19	0.25
Coefficient of Dynamic Friction (for Fabric)	1.56	0.99	0.83	1.77	1.76	0.93	0.96	1.41	0.75	0.22	0.66	0.26	0.62
Grin Performance	A	A	A	A	A	A	A	A	A	D	C	D	C
L^* Value	58.9	54.3	51.1	65.1	67.2	58.1	42.3	33.1	48.2	33.2	66.3	46.8	58.9
Color Fastness to Washing	4-5	4-5	4-5	4-5	4	4-5	4-5	3-4	3	3-4	4	3	4

[0151] As shown in Table 1 (here, El. denotes elastomer; Avg. denotes average), Examples 1 to 8 revealed to produce sea-island type composite multifilaments as well as ultrafine multifilaments efficiently obtained from the sea-island type composite multifilaments. Further, excellent spinnability and unwindability were exhibited by the sea-island type composite multifilament prepared in each of Examples 1 to 8.

[0152] Thanks to the use of polyamide-based elastomer resins each having a hardness in a specific range, the ultrafine multifilament of each of Examples 1 to 8 exhibited excellent grip performance with a coefficient of fiber-to-metal dynamic friction of 0.30 or more. Further, among them, ultrafine multifilaments with smaller single filament finenesses showed the tendency to have higher values in both the coefficient of fiber-to-metal dynamic friction and the coefficient of dynamic friction (for a fabric).

[0153] Moreover, a comparison of the ultrafine multifilaments having similar single filament finenesses revealed that, while the ultrafine multifilaments of Examples 1 to 7 and Comparative Examples 3 and 5 were dyed with the same dyeing agent, the ultrafine multi filaments of Examples 1, 6, and 7 had lower L* values than the ultrafine multifilament of either one of Comparative Examples 3 and 5. In particular, the ultrafine multifilament of Example 7 to which the amino group-containing color enhancer was added had an especially small L* value and thereby exhibited superior color development performance.

[0154] Furthermore, the ultrafine multifilament of each of Examples 1 to 8 exhibited advantageous color fastness to washing. The ultrafine multifilament of each of Examples 1 to 7, which comprised a polyamide-based elastomer, exhibited especially advantageous color fastness to washing.

[0155] In contrast, the sea-island type composite multifilament of Comparative Example 1, which had an excessively high island number, exhibited poor spinnability and unwindability. Also, the ultrafine multifilament prepared therefrom exhibited inadequate color fastness to washing. Moreover, the ultrafine multifilament of Comparative Example 1 exhibited poorer grip performance than any one of the Examples, despite the fact that the average single island diameter of the sea-island type composite multifilament of Comparative Example 1 was about a tenth of that of the sea-island type composite multifilament of Example 3 which had the largest average single island diameter,

[0156] The ultrafine multifilament of each of Comparative Examples 2 and 4, which comprised a non-elastomer resin as an island component resin, exhibited good spinnability and unwindability, but could not exhibit satisfactory grip performance. Further, despite having a similar single filament fineness to that of Example 1, the ultrafine multifilament of each of Comparative Examples 2 and 4 showed significantly lower values in both the coefficient of fiber-to-metal dynamic friction and the coefficient of dynamic friction (for a fabric) than the ultrafine multifilament of Example 1.

[0157] Furthermore, the ultrafine multifilament of each of Comparative Examples 3 and 5, which comprised a polyamide-based elastomer resin that did not have a hardness in a specific range as an island component resin, had a lower value of coefficient of dynamic friction than that of the ultrafine multifilament of Example 1 with a similar single filament fineness and thereby could not exhibit satisfactory grip performance.

INDUSTRIAL APPLICABILITY

[0158] An ultrafine multifilament comprising a thermoplastic elastomer can be efficiently formed from a sea-island type composite multifilament according to the present invention. The prepared ultrafine multifilament can exhibit excellent grip performance as an ultrafine fiber and is therefore suitable for use in, for example, a variety of clothing (e.g., outerwear, innerwear, uniforms, surgical gowns, patient gowns, nurse uniforms, work clothes, swimwear, skiwear, aprons, hats, belly bands, socks, gloves, and scarves), a variety of houseware (e.g., quilts, quilt covers, pillowcases, beds, bedspreads, blankets, sheets, bathmats, towels, tablecloths, curtains, shower curtains, nets, doorknob covers, diaper covers, and slippers), housing materials (e.g., carpets and curtains), industrial materials (e.g., nets, filters, and ropes), and agricultural, forestry and fishery materials (e.g., antiinsect and anti-weed nets, shading covers, and fishing nets).

[0159] Although the present invention has been fully described in connection with the preferred embodiments thereof with reference to the drawings, those skilled in the art will readily conceive numerous changes and modifications within the framework of obviousness of the present invention. Accordingly, such changes and modifications are, unless they depart from the scope of the present invention as delivered from the claims annexed hereto, to be construed as included therein.

Claims

1. A sea-island type composite multifilament comprising an island component and a sea component, the island component comprising a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less, the sea component comprising a water-soluble or easily alkali-soluble thermoplastic resin (B), and the sea-island type composite multifilament having an average single island diameter of 8000 nm or less.

2. The sea-island type composite multifilament according to claim 1, wherein the thermoplastic resin (B) of the sea component comprises a modified polyvinyl alcohol-based polymer in which a unit derived from an α-olefins and/or a vinyl ether is contained in a polyvinyl alcohol-based polymer moiety.

3. The sea-island type composite multifilament according to claim 1 or 2, wherein the number of islands in the sea-island type composite multifilament is from 3 to 200, and the sea-island type composite multifilament has a composite mass ratio (sea component: island component) between the sea component and the island component of from 20:80 to 70:30.

4. The sea-island type composite multifilament according to any one of claims 1 to 3, wherein the thermoplastic elastomer resin (A) comprises a polyamide-based elastomer resin or a polyester-based elastomer resin.

5. A fiber structure comprising, at least in part thereof, a sea-island type composite multifilament according to any one of claims 1 to 4 and/or a cut fiber thereof.

6. An ultrafine multifilament comprising a thermoplastic elastomer resin (A) having at least one of a Shore A hardness of 90 or less, a Shore D hardness of 60 or less, or a Rockwell hardness (R scale) of 70 or less, the ultrafine multifilament having a coefficient of fiber-to-metal dynamic friction of 0.30 or more.

7. The ultrafine multifilament according to claim 6, wherein the ultrafine multifilament has a single filament fineness of from 0.005 to 0.5 dtex.

8. An ultrafine fiber structure comprising, at least in part thereof, an ultrafine multifilament according to claim 6 or 7 and/or a cut fiber thereof.

9. The ultrafine fiber structure according to claim 8, wherein the ultrafine fiber structure comprises a woven fabric or a knitted fabric.

10. A process for producing an ultrafine multifilament, the process comprising at least a step of dissolving a thermoplastic resin (B) to be removed from a sea-island type composite multifilament according to any one of claims 1 to 4.

11. A process for producing an ultrafine fiber structure, the process comprising at least a step of dissolving a thermoplastic resin (B) to be removed from a fiber structure according to claim 5.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/000846

A. CLASSIFICATION OF SUBJECT MATTER

D01F 8/12(2006.01)i; ***D01F 6/00***(2006.01)i; ***D01F 8/10***(2006.01)i; ***D01F 8/14***(2006.01)i; ***D03D 15/33***(2021.01)i; ***D03D 15/56***(2021.01)i; ***D04B 1/18***(2006.01)i; ***D04B 21/00***(2006.01)i
FI: D01F8/12 Z; D01F8/10 C; D01F8/14 Z; D01F6/00 A; D03D15/33; D04B1/18; D04B21/00 B; D03D15/56

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)

D01F1/00-9/04, D03D1/00-27/18, D04B1/00-1/28, D04B21/00-21/20

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 1971-2022
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)

Japio-GPG/FX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 47-035324 B1 (UNION CARBIDE CORPORATION) 05 September 1972 (1972-09-05) claims, column 3, lines 14-17, column 3, line 39 to column 4, line 5, column 4, lines 35-39, column 14, lines 19-24, column 15, lines 22-26, example 11	6-9
Y	claims, column 5, lines 29-34, column 13, line 36 to column 14, line 18, column 14, lines 37-41	1-11
Y	JP 2019-189993 A (TORAY INDUSTRIES) 31 October 2019 (2019-10-31) paragraph [0013]	6-9
Y	JP 2014-25153 A (KURARAY CO LTD) 06 February 2014 (2014-02-06) claims, paragraphs [0032], [0033]	1-5, 10, 11
A	JP 2012-207220 A (TEIJIN FIBERS LTD) 25 October 2012 (2012-10-25)	1-11

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 March 2022	**22 March 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/JP2022/000846

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 47-035324 B1	05 September 1972	(Family: none)	
JP 2019-189993 A	31 October 2019	(Family: none)	
JP 2014-25153 A	06 February 2014	(Family: none)	
JP 2012-207220 A	25 October 2012	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2021004876 A **[0001]**
- JP 2014101613 A **[0004]**