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(54) **CORE-SHEATH COMPOSITE FIBER FOR ARTIFICIAL HAIR AND HEADDRESS PRODUCT COMPRISING SAME**

(57) The present invention, in one embodiment, relates to core-sheath conjugate fibers for artificial hair comprising a core part and a sheath part. The fibers have a core-to-sheath area ratio of core:sheath = 2:8 to 7:3, an eccentricity of 5% or more, and a flat multilobed shape in cross section. In the fiber cross section, a ratio of a length of a major axis of the fiber cross section to a length of a first minor axis of the fiber cross section is 1.10 or more and 3.00 or less, and a ratio of a length of a major axis of the core part to a length of a first minor axis of the core part is 1.10 or more and 3.00 or less. A direction of the major axis of the fiber cross section and a direction of the major axis of the core part substantially coincide with each other. The present invention further relates to hair ornament products comprising the core-sheath conjugate fibers for artificial hair. Thus, the present invention provides core-sheath conjugate fibers for artificial hair having touch and appearance close to human hair, exhibiting favorable curling property without the need for curl setting and having extremely high curl retentive property, and hair ornament products including the same.

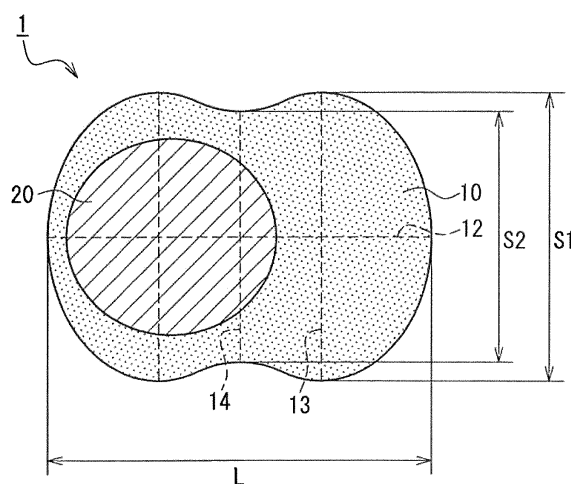


FIG. 3

Description

Technical Field

- 5 **[0001]** The present invention relates to core-sheath conjugate fibers for artificial hair that can be used as an alternative to human hair, and hair ornament products including the same.

Background Art

- 10 **[0002]** Conventionally, human hair has been used for hair ornament products such as hairpieces, hair wigs, hair extensions, hair bands, and doll hair. In recent years, however, the cost of human hair increases due to difficulty in obtaining human hair, and a demand for artificial hair that can be substituted for human hair increases accordingly. Examples of synthetic fibers used for artificial hair include acrylic fibers, vinyl chloride-based fibers, vinylidene chloride-based fibers, polyester-based fibers, polyamide-based fibers, and polyolefin-based fibers.

- 15 **[0003]** Artificial hair is required to have touch and appearance close to human hair. For example, Patent Document 1 proposes, as fibers for artificial hair having appearance, touch, and feel such as texture close to natural hair, core-sheath conjugate fibers comprising a semi-aromatic polyamide component in the core part and a linear saturated aliphatic polyamide component in the sheath part.

- 20 **[0004]** Artificial hair is also required to have curl setting property and curl retentive property. It has been attempted to improve these characteristics by controlling the materials and cross-sectional shape of fibers. However, this attempt needs to be balanced with costs and other physical properties required for artificial hair such as touch and feel, and it is difficult to reduce the change in strength and the loosening of curls with time due to its own weight just by setting curls using a hair iron or hot water.

- 25 **[0005]** Further, unlike human hair, when artificial hair made of thermoplastic resin is curled with a hair iron, it is necessary to perform cooling including holding fibers by hand after curling until the fibers reach a temperature equal to or less than its glass transition point so as not to collapse the curl shape, and therefore, it has been desired to improve the curl setting property and curl retentive property of artificial hair. For example, Patent Document 2 discloses, as fibers having excellent curl retentive property, fibers for artificial hair comprising core-sheath type vinylidene chloride-based conjugate fibers whose core-sheath phase comprising a vinylidene chloride-based resin phase and a thermoplastic resin phase having a density of 0.85 to 1.00 g/cc.

Prior Art Documents

Patent Documents

- 35 **[0006]**

Patent Document 1: WO 2006/087911

Patent Document 2: JP 2002-129432 A

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Disclosure of Invention

Problem to be Solved by the Invention

- 45 **[0007]** The fibers described in Patent Document 1 have feel close to natural hair because of its core-sheath structure, but curl setting including cooling is necessary so as to impart a curled style to the fibers. Further, the curls of the fibers mostly loosen when they get wet, and the loosened curls do not perfectly return to its originally curled state even when they are dried. These fibers are inferior in the curl retentive property. The fibers of Patent Document 2 have improved curl retentive property as compared with fibers consisting only of vinylidene chloride, but loosening of curls due to its own weight is unavoidable, and the fibers also require curl setting including the above cooling.

- 50 **[0008]** In order to solve the above problems, the present invention provides core-sheath conjugate fibers for artificial hair having touch and appearance close to human hair, exhibiting favorable curling property without the need for curl setting and having extremely high curl retentive property, and hair ornament products including the same.

- 55 **Means for Solving Problem**

- [0009]** In one embodiment, the present invention relates to a core-sheath conjugate fiber for artificial hair comprising a core part and a sheath part. The core-sheath conjugate fiber for artificial hair has a core-to-sheath area ratio of

core:sheath = 2:8 to 7:3 and an eccentricity of 5% or more. The core-sheath conjugate fiber for artificial hair has a flat multilobed shape in cross section. In the fiber cross section, a ratio of a length of a major axis of the fiber cross section to a length of a first minor axis of the fiber cross section is 1.10 or more and 3.00 or less. The major axis of the fiber cross section is a longest straight line among a symmetrical axis of the fiber cross section and straight lines that connect any two points on an outer circumference of the fiber cross section and that extend parallel to the symmetrical axis of the fiber cross section. The first minor axis of the fiber cross section is a longest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section. In the fiber cross section, a ratio of a length of a major axis of the core part to a length of a first minor axis of the core part is 1.10 or more and 3.00 or less. The major axis of the core part is a longest straight line among a symmetrical axis of the core part and straight lines that connect any two points on an outer circumference of the core part and that extend parallel to the symmetrical axis of the core part. The first minor axis of the core part is a longest straight line formed when any two points on the outer circumference of the core part are connected perpendicular to the major axis of the core part. A direction of the major axis of the fiber cross section and a direction of the major axis of the core part substantially coincide with each other.

[0010] It is preferred that in the fiber cross section, a ratio of a length of a second minor axis of the fiber cross section to the length of the first minor axis of the fiber cross section is 0.50 or more and less than 1.00. The second minor axis of the fiber cross section is a shortest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section.

[0011] It is preferred that the flat multilobed shape is a flat two-lobed shape in which two circles, two ellipses, or one circle and one ellipse are connected via recesses.

[0012] It is preferred that the core-sheath conjugate fiber for artificial hair comprises at least one resin composition selected from the group consisting of a polyester-based resin composition, a polyamide-based resin composition, a vinyl chloride-based resin composition, a modacrylic-based resin composition, a polycarbonate-based resin composition, a polyolefin-based resin composition, and a polyphenylene sulfide-based resin composition. Further, it is preferred that the core part and/or sheath part of the core-sheath conjugate fiber for artificial hair comprises a polyester-based resin composition comprising at least one polyester-based resin selected from the group consisting of polyalkylene terephthalate and a copolymerized polyester comprising polyalkylene terephthalate as a main component. Further, it is preferred that the core part and/or sheath part of the core-sheath conjugate fiber for artificial hair comprises a polyamide-based resin composition comprising polyamide-based resin comprising at least one selected from the group consisting of nylon 6 and nylon 66 as a main component.

[0013] In one embodiment, the present invention further relates to a hair ornament product comprising the above core-sheath conjugate fiber for artificial hair.

[0014] The hair ornament product may be any one selected from the group consisting of a hair wig, a hairpiece, weaving hair, a hair extension, braided hair, a hair accessory, and doll hair.

Effects of the Invention

[0015] The present invention can provide core-sheath conjugate fibers for artificial hair having touch and appearance close to human hair, exhibiting favorable curling property without the need for curl setting and having extremely high curl retentive property, and hair ornament products including the same.

Brief Description of Drawings

[0016]

[FIG. 1] FIG. 1 is a schematic diagram showing a fiber cross section of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention.

[FIG. 2] FIG. 2 is a schematic diagram illustrating the eccentricity of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention.

[FIG. 3] FIG. 3 is a schematic diagram illustrating a length of a major axis of a fiber cross section, a length of a first minor axis of the fiber cross section, and a length of a second minor axis of the fiber cross section in the fiber cross section of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention.

[FIG. 4] FIG. 4 is a schematic diagram illustrating a length of a major axis of a core part and a length of a first minor axis of the core part in a fiber cross section of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention.

[FIG. 5] FIG. 5 is a laser micrograph (400x magnification) of fiber cross sections of fibers of Example 3.

[FIG. 6] FIG. 6 is a laser micrograph (400x magnification) of fiber cross sections of fibers of Comparative Example 1.

[FIG. 7] FIG. 7 is a laser micrograph (400x magnification) of fiber cross sections of fibers of Comparative Example 5.

[FIG. 8] FIG. 8 is a laser micrograph (400x magnification) of fiber cross sections of fibers of Comparative Example 6.

Description of the Invention

[0017] The present inventors conducted intensive studies to solve the above problems and found out that core-sheath conjugate fibers for artificial hair having touch and appearance (gloss) close to human hair, exhibiting favorable curling property without the need for curl setting and having extremely high curl retentive property, are realized with the following configuration. In core-sheath conjugate fibers having a core-to-sheath area ratio of core:sheath = 2:8 to 7:3 and an eccentricity (also called eccentric degree) of 5% or more, the fiber cross section has a flat multilobed shape. In the fiber cross section, a ratio of a length of a major axis of the fiber cross section to a length of a first minor axis of the fiber cross section is 1.10 or more and 3.00 or less. The major axis of the fiber cross section is a longest straight line among symmetrical axes of the fiber cross section and straight lines that connect any two points on an outer circumference of the fiber cross section and that extend parallel to the symmetrical axes of the fiber cross section, and the first minor axis of the fiber cross section is a longest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section. Further, in the fiber cross section, a ratio of a length of a major axis of the core part to a length of a first minor axis of the core part is 1.10 or more and 3.00 or less. The major axis of the core part is a longest straight line among symmetrical axes of the core part and straight lines that connect any two points on an outer circumference of the core part and that extend parallel to the symmetrical axes of the core part, and the first minor axis of the core part is a longest straight line formed when any two points on the outer circumference of the core part are connected perpendicular to the major axis of the core part. A direction of the major axis of the fiber cross section and a direction of the major axis of the core part substantially coincide with each other. Thus, the present invention has been achieved. The core-sheath conjugate fibers for artificial hair having the above configuration can prevent the separation of fibers and the exposure of the core part to the surface due to separation of the core part and the sheath part while having latent crimpability and curls by natural crimp derived from the fiber structure, thereby exhibiting favorable curling property without the need for curl setting and extremely high curl retentive property.

[0018] The core-sheath conjugate fibers for artificial hair each comprise a core part and a sheath part and have a flat multilobed shape in cross section. The flat multilobed shape may be, but is not particularly limited to, a lobed shape in which two or more selected from a group consisting of circle and ellipse are connected via recesses. The number of lobes may be 2 to 10, or 2 to 8. In terms of productivity, the flat multilobed shape is preferably a flat two-lobed shape in which two circles, two circles, or one circle and one ellipse are connected via recesses. The circle or ellipse does not need to form a continuous arc, and may be a substantial circle or ellipse that is modified partially (excluding an acute angle). Note here that it is unnecessary to take into consideration asperities of 2 μm or less generated on the outer circumference of the fiber cross section due to the use of additives, etc.

[0019] Since the core-sheath conjugate fibers for artificial hair have a flat multilobed fiber cross section, they have favorable curling property without the need for curl setting. Further, since the core-sheath conjugate fibers for artificial hair have a flat multilobed fiber cross section, each fiber surface has recesses and projections, so that the flat area decreases and reflection of light decreases on the fiber surface. Specifically, when the core-sheath conjugate fibers for artificial hair have a flat two-lobed cross-sectional shape in which two circles, two ellipses, or one circle and one ellipse are connected via recesses, four projections in total are present on both sides of the two recesses. With this configuration, reflection of light decreases, and the fibers tend to have gloss approximate to human hair.

[0020] FIG. 1 is a schematic diagram showing a fiber cross section of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention. A core-sheath conjugate fiber for artificial hair 1 of this embodiment comprises a sheath part 10 and a core part 20, and the fiber cross section has a flat two-lobed shape in which two ellipses are connected via recesses.

[0021] The core-sheath conjugate fiber for artificial hair has a core-to-sheath area ratio in a range of core:sheath = 2:8 to 7:3. If the core part is smaller than this range, the core part cannot fully develop its function, and fibers with natural crimp cannot be obtained. Conversely, if the core part is larger than this range, the sheath part cannot fully develop its function. Fibers cannot obtain natural crimpability while the sheath part cannot cover the entire core part. Consequently, the core part is exposed to the fiber surface, and the two components separate. This makes it difficult to form conjugate fibers. In terms of improving the curling property by natural crimp, the core-sheath conjugate fiber for artificial hair has a core-to-sheath area ratio in a range of core:sheath = 3:7 to 6:4.

[0022] The core-sheath conjugate fiber for artificial hair has an eccentricity of 5% or more, preferably 5% or more and 50% or less, and more preferably 10% or more and 30% or less. By setting the eccentricity within the above range, it is possible to obtain fibers with natural crimpability while preventing the core part from being exposed to the fiber surface.

[0023] The eccentricity of the core-sheath conjugate fiber for artificial hair can be calculated from the following formula based on the length of the major axis of the fiber cross section and the distance between the central point of the major axis of the fiber cross section and the central point of the major axis of the core part in the fiber cross section.

Eccentricity (%) = Distance between the central point of the major axis of the
 fiber cross section and the central point of the major axis of the core part / (Length of
 the major axis of the fiber cross section / 2) x 100

[0024] In the core-sheath conjugate fiber for artificial hair, the major axis of the fiber cross section refers to a longest straight line among symmetrical axes of the fiber cross section and straight lines that connect any two points on an outer circumference of the fiber cross section and that extend parallel to the symmetrical axes of the fiber cross section. Further, the major axis of the core part refers to a longest straight line in the core part among symmetrical axes of the core part and straight lines that connect any two points on an outer circumference of the core part and that extend parallel to the symmetrical axes of the core part.

[0025] FIG. 2 is a schematic diagram illustrating the eccentricity of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention. As illustrated in FIG. 2, a core-sheath conjugate fiber for artificial hair 1 of this embodiment comprises a sheath part 10 and a core part 20, and has a flat two-lobed shape in cross section. The eccentricity of the fiber is expressed by the following formula, where L represents a length of a major axis 12 of the fiber cross section, and d represents a distance between a central point 11 of the major axis of the fiber cross section and a central point 21 of the major axis of the core part.

$$\text{Eccentricity (\%)} = d/(L/2) \times 100$$

[0026] In the fiber cross section of the core-sheath conjugate fiber for artificial hair, a ratio of the length of the major axis of the fiber cross section to a length of a first minor axis of the fiber cross section is 1.10 or more and 3.00 or less, preferably 1.15 or more and 2.50 or less, and more preferably 1.20 or more and 2.00 or less. The first minor axis of the fiber cross section is a longest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section. When the ratio of the length of the major axis of the fiber cross section to the length of the first minor axis of the fiber cross section is within the above range, fibers can keep favorable touch and appearance. Further, when the ratio of the length of the major axis of the fiber cross section to the length of the first minor axis of the fiber cross section is 1.10 or more, fibers are hardly tangled, and the combing property improves. If there are two or more longest straight lines formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section, one of them is defined as the first minor axis.

[0027] In the fiber cross section of the core-sheath conjugate fiber for artificial hair, a ratio of a length of a second minor axis of the fiber cross section to the length of the first minor axis of the fiber cross section is preferably 0.50 or more and less than 1.00, more preferably 0.65 or more and less than 1.00, and further preferably 0.80 or more and less than 1.00. The second minor axis of the fiber cross section is a shortest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section. When the ratio of the length of the second minor axis to the length of the first minor axis is 0.50 or more, fibers can have soft and good touch. When the ratio of the length of the second minor axis to the length of the first minor axis is less than 1.00, the flat area on the fiber surface decreases and reflection of light on the fiber surface decreases, whereby fibers tend to have gloss approximate to human hair.

[0028] FIG. 3 is a schematic diagram illustrating the length of the major axis of the fiber cross section, the length of the first minor axis of the fiber cross section, and the length of the second minor axis of the fiber cross section in the fiber cross section of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention. As illustrated in FIG. 3, a core-sheath conjugate fiber for artificial hair 1 of this embodiment comprises a sheath part 10 and a core part 20, and has a flat two-lobed shape in cross section. As illustrated in FIG. 3, in the fiber cross section, the major axis of the fiber cross section is a longest straight line 12 among symmetrical axes of the fiber cross section and straight lines that connect any two points on an outer circumference of the fiber cross section and that extend parallel to the symmetrical axes of the fiber cross section, and the first minor axis of the fiber cross section is a longest straight line 13 formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis 12 of the fiber cross section, and the second minor axis of the fiber cross section is a shortest straight line 14 formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis 12 of the fiber cross section.

[0029] In the core-sheath conjugate fiber for artificial hair 1 of this embodiment, a ratio (L/S1) of a length L of the major axis 12 of the fiber cross section to a length S1 of the first minor axis of the fiber cross section is 1.10 or more and 3.00

or less, more preferably 1.15 or more and 2.50 or less, and further preferably 1.20 or more and 2.00 or less. When the ratio of the length of the major axis of the fiber cross section to the length of the first minor axis of the fiber cross section is within the above range, fibers can keep favorable touch and appearance.

[0030] In the core-sheath conjugate fiber for artificial hair 1 of this embodiment, a ratio (S_2/S_1) of a length S_2 of a second minor axis 14 of the fiber cross section to a length S_1 of the first minor axis 13 of the fiber cross section is preferably 0.50 or more and less than 1.00, more preferably 0.65 or more and less than 1.00, and further preferably 0.80 or more and less than 1.00.

[0031] In the core-sheath conjugate fibers for artificial hair, "the ratio of the length of the major axis of the fiber cross section to the length of the first minor axis of the fiber cross section" is an average ratio in 30 fiber cross sections selected randomly. Preferably, in the 30 fiber cross sections selected randomly, a maximum value and a minimum value among the ratios of the length of the major axis of the fiber cross section to the length of the first minor axis of the fiber cross section are both within the above range. Further, in the core-sheath conjugate fibers for artificial hair, "the ratio of the length of the second minor axis of the fiber cross section to the length of the first minor axis of the fiber cross section" is an average ratio in 30 fiber cross sections selected randomly. Preferably, in the 30 fiber cross sections selected randomly, a maximum value and a minimum value among the ratios of the length of the second minor axis of the fiber cross section to the length of the first minor axis of the fiber cross section are both within the above range.

[0032] In the fiber cross section of the core-sheath conjugate fiber for artificial hair, a ratio of a length of a major axis of the core part to a length of a first minor axis of the core part is 1.10 or more and 3.00 or less, preferably 1.15 or more and 2.50 or less, and more preferably 1.20 or more and 2.00 or less. The major axis of the core part is a longest straight line among symmetrical axes of the core part and straight lines that connect any two points on an outer circumference of the core part and that extend parallel to the symmetrical axes of the core part. The first minor axis of the core part is a longest straight line formed when any two points on the outer circumference of the core part are connected perpendicular to the major axis of the core part. Further, the core-sheath conjugate fiber for artificial hair is configured so that a direction of the major axis of the fiber cross section and a direction of the major axis of the core part substantially coincide with each other. When the direction of the major axis of the fiber cross section and the direction of the major axis of the core part substantially coincide with each other, and the ratio of the length of the major axis of the core part to the length of the first minor axis of the core part are within the above range, the outer circumferential shape of the fiber cross section and the outer circumferential shape of the core part are close to each other in the fiber cross section. Thus, it is possible to prevent the separation of fibers due to separation of the two components and the exposure of the core part to the surface while keeping favorable touch and appearance as artificial hair. Moreover, a change in shape between an extruded shape from a nozzle and a fiber cross-sectional shape after spinning becomes small, which is advantageous in a spinning processing in that a nozzle design for realizing the above cross-sectional shape becomes easily. Further, since the direction of the major axis of the fiber cross section and the direction of the major axis of the core part substantially coincide with each other, the anisotropy of the bending elastic modulus derived from the geometrical moment of inertia also coincide between the whole fiber and the core part. Thus, it is possible to easily adjust qualities necessary for artificial hair such as touch and combing property.

[0033] In the core-sheath conjugate fibers for artificial hair, the cross-sectional shape of the core part is not particularly limited as long as the ratio of the length of the major axis of the core part to the length of the first minor axis of the core part is within the above range, and the direction of the major axis of the fiber cross section and the direction of the major axis of the core part substantially coincide with each other. However, it is preferred that the cross-sectional shape of the core part is elliptic, a flat multilobed shape such as a flat two-lobed shape, etc.

[0034] FIG. 4 is a schematic diagram illustrating the length of the major axis of the core part and the length of the first minor axis of the core part in a fiber cross section of a core-sheath conjugate fiber for artificial hair in one embodiment of the present invention. As illustrated in FIG. 4, a core-sheath conjugate fiber for artificial hair 1 of this embodiment comprises a sheath part 10 and a core part 20, and has a flat two-lobed shape in cross section. As illustrated in FIG. 4, in the fiber cross section, the major axis of the core part is a longest straight line 22 in the core part among symmetrical axes of the core part and straight lines that connect any two points on an outer circumference of the core part and that extend parallel to the symmetrical axes of the core part, and the first minor axis of the core part is a longest straight line 23 formed when any two points on the outer circumference of the core part are connected perpendicular to the major axis 22 of the core part.

[0035] In the core-sheath conjugate fiber for artificial hair 1 of this embodiment, a ratio (L_c/S_c) of a length L_c of the major axis 22 of the core part to a length S_c of the first minor axis 23 of the core part is 1.10 or more and 3.00 or less, preferably 1.15 or more and 2.50 or less, and more preferably 1.20 or more and 2.00 or less.

[0036] In the core-sheath conjugate fiber for artificial hair, "the ratio of the length of the major axis of the core part to the length of the first minor axis of the core part" is an average ratio in 30 fiber cross sections selected randomly. Preferably, in the 30 fiber cross sections selected randomly, a maximum value and a minimum value among the ratios of the length of the major axis of the core part to the length of the first minor axis of the core part are both within the above range.

[0037] If the ratio of the length of the major axis of the core part to the length of the first minor axis of the core part is not within the above range, or the direction of the major axis of the fiber cross section and the direction of the major axis of the core part do not substantially coincide with each other, a variation in the thickness of the sheath in the fiber cross section becomes large. This may cause the separation of the two components, or largely change the shape between the extruded shape from a nozzle and the fiber cross-sectional shape after spinning, which makes the spinning processing more difficult. Further, the core part cannot fully develop its function, and fibers with natural crimp cannot be obtained.

[0038] It is unnecessary that all of the core-sheath conjugate fibers for artificial hair have the same fineness and cross-sectional shape. They may be a mixture of fibers having different finenesses and cross-sectional shapes. Further, in the fiber cross section of the core-sheath conjugate fibers for artificial hair, in order to prevent the separation of the core part and the sheath part, it is preferred that the core part is not exposed to the fiber surface and completely covered with the sheath part.

[0039] The composition of the core-sheath conjugate fibers for artificial hair is not particularly limited. For example, the core-sheath conjugate fibers for artificial hair may comprise a resin composition such as a polyester-based resin composition, a polyamide-based resin composition, a vinyl chloride-based resin composition, a modacrylic-based resin composition, a polycarbonate-based resin composition, a polyolefin-based resin composition, and a polyphenylene sulfide-based resin composition. These resin compositions may be used in combination of two or more kinds. A flame retardant may be used together in terms of flame resistance. A polyester-based resin composition comprising polyester-based resin and a bromine-based polymeric flame retardant, a polyamide-based resin composition comprising polyamide-based resin and a bromine-based polymeric flame retardant, etc., are preferably used.

[0040] In terms of heat resistance and flame resistance, the core part and/or sheath part of the core-sheath conjugate fibers for artificial hair preferably comprises a polyester-based resin composition comprising polyester resin and a bromine-based polymeric flame retardant. Specifically, the core-sheath conjugate fibers for artificial hair may be obtained by melt spinning a polyester-based resin composition comprising polyester resin and a bromine-based polymeric flame retardant. More preferably, the core-sheath conjugate fibers for artificial hair comprise a polyester-based resin composition comprising 100 parts by weight of at least one polyester resin selected from the group consisting of polyalkylene terephthalate and a copolymerized polyester comprising polyalkylene terephthalate as a main component and 5 parts by weight or more and 40 parts by weight or less of a bromine-based polymeric flame retardant.

[0041] Examples of the polyalkylene terephthalate include, but are not particularly limited to, polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, and polycyclohexane dimethylene terephthalate. Examples of the copolymerized polyester comprising polyalkylene terephthalate as a main component include, but are not particularly limited to, copolymerized polyesters comprising polyalkylene terephthalate such as polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate or polycyclohexane dimethylene terephthalate, as a main component and other copolymerizable components. In one embodiment of the present invention, the term "copolymerized polyester comprising polyalkylene terephthalate as a main component" refers to a copolymerized polyester comprising 80 mol% or more of polyalkylene terephthalate.

[0042] Examples of the other copolymerizable component include: polycarboxylic acids such as isophthalic acid, orthophthalic acid, naphthalenedicarboxylic acid, paraphenylenedicarboxylic acid, trimellitic acid, pyromellitic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, and dodecanedioic acid, and their derivatives; dicarboxylic acids including a sulfonic acid salt such as 5-sodiumsulfoisophthalic acid and dihydroxyethyl 5-sodiumsulfoisophthalate, and their derivatives; 1,2-propanediol; 1,3-propanediol; 1,4-butanediol; 1,6-hexanediol; neopentyl glycol; 1,4-cyclohexanedimethanol; diethylene glycol; polyethylene glycol; trimethylolpropane; pentaerythritol; 4-hydroxybenzoic acid; ϵ -caprolactone; and ethylene glycol ether of bisphenol A.

[0043] In terms of stability and simplicity of operation, the copolymerized polyester is preferably produced by adding a small amount of the other copolymerizable component to polyalkylene terephthalate as a main component to react. The polyalkylene terephthalate may be a polymer of terephthalic acid and/or a derivative thereof (e.g., methyl terephthalate) and alkylene glycol. The copolymerized polyester may be produced by polymerizing a composition comprising a monomer or oligomer component as the small amount of the other copolymerizable component, and a mixture of terephthalic acid and/or a derivative thereof (e.g., methyl terephthalate) and alkylene glycol used for polymerization of polyalkylene terephthalate as a main component.

[0044] The copolymerized polyester may be any copolymerized polyester in which the other copolymerizable component is polycondensed to the main chain and/or side chain of polyalkylene terephthalate as a main component. The copolymerization method is not particularly limited.

[0045] Specific examples of the copolymerized polyester comprising polyalkylene terephthalate as a main component include copolymerized polyesters obtained by copolymerizing polyethylene terephthalate as a main component with one compound selected from the group consisting of ethylene glycol ether of bisphenol A, 1,4-cyclohexanedimethanol, isophthalic acid, and dihydroxyethyl 5-sodiumsulfoisophthalate.

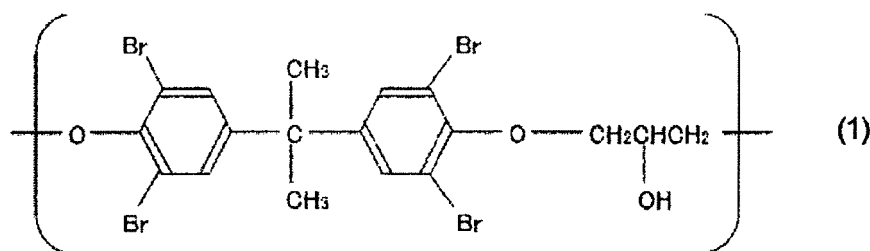
[0046] The polyalkylene terephthalate and the copolymerized polyester comprising polyalkylene terephthalate as a main component may be used individually or in combinations of two or more. Particularly, it is preferable to use the

following individually or in combinations of two or more: polyethylene terephthalate; polypropylene terephthalate; polybutylene terephthalate; a copolymerized polyester obtained by copolymerizing polyethylene terephthalate as a main component with ethylene glycol ether of bisphenol A; a copolymerized polyester obtained by copolymerizing polyethylene terephthalate as a main component with 1,4-cyclohexanedimethanol; a copolymerized polyester obtained by copolymerizing polyethylene terephthalate as a main component with isophthalic acid; and a copolymerized polyester obtained by copolymerizing polyethylene terephthalate as a main component with dihydroxyethyl 5-sodiumsulfoisophthalate.

[0047] An intrinsic viscosity (IV value) of the polyester resin is not particularly limited, but is preferably 0.3 or more and 1.2 or less, and more preferably 0.4 or more and 1.0 or less. When the intrinsic viscosity is 0.3 or more, fibers to be obtained can have adequate mechanical strength, and there is no risk of dripping during a combustion test. Further, when the intrinsic viscosity is 1.2 or less, the molecular weight does not increase too much, and the melt viscosity does not become too high. This facilitates melt spinning and tends to uniform the fineness.

[0048] The bromine-based polymeric flame retardant is not particularly limited but preferably a brominated epoxy-based flame retardant in terms of heat resistance and flame resistance. The brominated epoxy-based flame retardant may use as a raw material a brominated epoxy-based flame retardant having an epoxy group or tribromophenol at the end of the molecule. It is preferred that the structure of the brominated epoxy-based flame retardant after melt kneading has, but is not particularly limited to, 80 mol% or more of the constitutional unit represented by the following chemical formula (1), where the total amount of the constitutional unit represented by the chemical formula (1) and another constitutional unit in which at least part of the chemical formula (1) is modified is 100 mol%. The structure of the brominated epoxy-based flame retardant at the end of the molecule may be changed after melt kneading. For example, the end of the molecule of the brominated epoxy-based flame retardant may be replaced by a group other than the epoxy group or tribromophenol, such as a hydroxyl group, a phosphoric acid group, or a phosphonic acid group. Alternatively, the end of the molecule of the brominated epoxy-based flame retardant may be bound to a polyester component through an ester group.

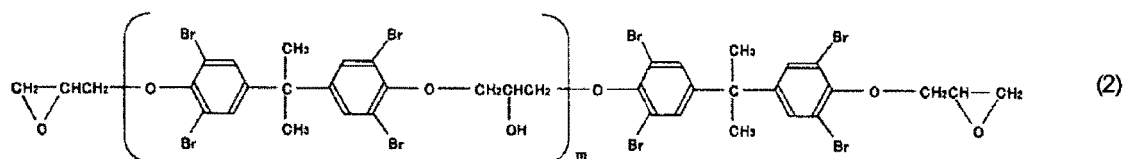
[Chemical formula 1]



[0049] Moreover, part of the structure of the brominated epoxy-based flame retardant, except for the end of the molecule, may be changed. For example, the brominated epoxy-based flame retardant may have a branched structure in which the secondary hydroxyl group and the epoxy group are bound. Also, part of the bromine of the chemical formula (1) may be eliminated or added, as long as the bromine content in the molecule of the brominated epoxy-based flame retardant is not changed significantly.

[0050] The brominated epoxy-based flame retardant is preferably a polymeric brominated epoxy-based flame retardant as represented by the following general formula (2), for example. In the general formula (2) below, m is 1 to 1000. The polymeric brominated epoxy-based flame retardant represented by the general formula (2) may be a commercially available product such as a brominated epoxy-based flame retardant (trade name "SR-T2MP") manufactured by SAKAMOTO YAKUHI KOGYO CO., LTD.

[Chemical formula 2]



[0051] The polyamide-based resin used in the present invention refers to nylon resin obtained by polymerizing at least one selected from the group consisting of lactam, aminocarboxylic acid, a mixture of dicarboxylic acid and diamine, a mixture of dicarboxylic acid derivative and diamine, and a salt of dicarboxylic acid and diamine.

[0052] Specific examples of the lactam include, but are not particularly limited to, 2-azetidinone, 2-pyrrolidinone, δ -valerolactam, ϵ -caprolactam, enantholactam, capryllactam, undecalactam, and laulolactam. Among these, ϵ -caprolactam, undecalactam and laulolactam are preferred, and ϵ -caprolactam is particularly preferred. These lactams may be used individually or in combinations of two or more.

[0053] Specific examples of the aminocarboxylic acid include, but are not particularly limited to, 6-aminocaproic acid, 7-aminoheptanoic acid, 8-aminooctanoic acid, 9-aminononanoic acid, 10-aminodecanoic acid, 11-aminoundecanoic acid, and 12-aminododecanoic acid. Among these, 6-aminocaproic acid, 11-aminoundecanoic acid and 12-aminododecanoic acid are preferred, and 6-aminocaproic acid is particularly preferred. These aminocarboxylic acids may be used individually or in combinations of two or more.

[0054] Specific examples of the dicarboxylic acid used in the mixture of dicarboxylic acid and diamine, the mixture of dicarboxylic acid derivative and diamine, or the salt of dicarboxylic acid and diamine include, but are not particularly limited to, aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, brassylic acid, tetradecanedioic acid, pentadecanedioic acid, octadecanedioic acid; alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid; and aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, and naphthalenedicarboxylic acid. Among these, adipic acid, sebacic acid, dodecanedioic acid, terephthalic acid and isophthalic acid are preferred, and adipic acid, terephthalic acid and isophthalic acid are particularly preferred. These dicarboxylic acids may be used individually or in combinations of two or more.

[0055] Specific examples of the diamine used in the mixture of dicarboxylic acid and diamine, the mixture of dicarboxylic acid derivative and diamine, or the salt of dicarboxylic acid and diamine include, but are not particularly limited to, aliphatic diamines such as 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 2-methyl-1,5-diaminopentane (MDP), 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane, 1,10-diaminodecane, 1,11-diaminoundecane, 1,12-diaminododecane, 1,13-diaminotridecane, 1,14-diaminotetradecane, 1,15-diaminopentadecane, 1,16-diaminohexadecane, 1,17-diaminoheptadecane, 1,18-diaminooctadecane, 1,19-diaminononadecane, and 1,20-diaminoeicosane; alicyclic diamines such as cyclohexanediamine, and bis-(4-aminohexyl)methane; and aromatic diamines such as m-xylylenediamine, and p-xylylenediamine. Among these, aliphatic diamines are preferred, and hexamethylenediamine is particularly preferred. These diamines may be used individually or in combinations of two or more.

[0056] Examples of the polyamide-based resin (nylon resin) include, but are not particularly limited to, nylon 6, nylon 66, nylon 11, nylon 12, nylon 6-10, nylon 6-12, semi-aromatic nylons comprising a unit of nylon 6T and/or 6I, and copolymers of these nylon resins. In particular, nylon 6, nylon 66, and copolymers of nylon 6 and nylon 66 are more preferred.

[0057] The polyamide-based resin can be produced, for example, by a polyamide-based resin polymerization method that includes heating a raw material of polyamide-based resin in the presence or absence of a catalyst. Stirring may or may not be performed during the polymerization, but it is preferable to perform stirring to obtain a homogeneous product. The polymerization temperature can be set optionally in accordance with the polymerization degree of a target polymerized product, the reaction yield, and the reaction time, but a lower temperature is preferred in terms of the quality of resultant polyamide-based resin. The reaction rate can also be set optionally. The polymerization pressure is not particularly limited, but it is preferable to reduce the pressure in the system to efficiently extract a volatile component out of the system.

[0058] The terminal groups of polyamide-based resin used in the present invention may be end-capped with a carboxylic acid compound or an amine compound as needed. When monocarboxylic acid and/or monoamine is used for end-capping, the terminal amino group concentration or terminal carboxyl group concentration of the obtained nylon resin is reduced as compared with the case of not using the end-capping agent. Meanwhile, when dicarboxylic acid or diamine is used for end-capping, the sum of the terminal amino group concentration and the terminal carboxyl group concentration does not change, but the ratio of the terminal amino group concentration to the terminal carboxyl group concentration changes.

[0059] Specific examples of the carboxylic acid compound include, but are not particularly limited to, aliphatic monocarboxylic acids such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, myristoleic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, and arachic acid; alicyclic monocarboxylic acids such as cyclohexanecarboxylic acid and methylcyclohexanecarboxylic acid; aromatic monocarboxylic acids such as benzoic acid, toluic acid, ethylbenzoic acid, and phenylacetic acid; aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, brassylic acid, tetradecanedioic acid, pentadecanedioic acid, octadecanedioic acid; alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid; and aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, and naphthalenedi-

carboxylic acid.

[0060] Specific examples of the amine compound include, but are not particularly limited to, aliphatic monoamines such as butylamine, pentylamine, hexylamine, heptylamine, octylamine, 2-ethylhexylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, octadecylamine, nonadecylamine, and icosylamine; alicyclic monoamines such as cyclohexylamine and methylcyclohexylamine; aromatic monoamines such as benzylamine and β -phenylethylamine; aliphatic diamines such as 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane, 1,10-diaminodecane, 1,11-diaminoundecane, 1,12-diaminododecane, 1,13-diaminotridecane, 1,14-diaminotetradecane, 1,15-diaminopentadecane, 1,16-diaminohexadecane, 1,17-diaminoheptadecane, 1,18-diaminooctadecane, 1,19-diaminononadecane, and 1,20-diaminoeicosane; alicyclic diamines such as cyclohexanediamine and bis-(4-aminohexyl)methane; and aromatic diamines such as xylylenediamine.

[0061] The terminal group concentration of the polyamide-based resin is not specifically limited. However, when it is necessary to increase dye-affinity for fiber application, or when a material suitable for alloying is designed for resin application, it is preferred that the terminal amino group concentration is high. On the other hand, when it is desired to prevent coloration or gelation under long-term aging conditions, it is rather preferred that the terminal amino group concentration is low. Further, when it is desired to prevent breakage in melt-spinning the polyamide-based resin, which may be caused by the lactam reproduction and the oligomer production in re-melting, in-mold deposition in continuous injection molding, and formation of die marks in continuous extrusion of films, it is preferred that the terminal carboxyl group concentration and the terminal amino group concentration in the polyamide-based resin are both low. Depending on the use of the polyamide-based resin, the terminal group concentration can be controlled. Both of the terminal amino group concentration and the terminal carboxyl group concentration in the polyamide-based resin are preferably from 1.0×10^{-5} to 15.0×10^{-5} eq/g, more preferably from 2.0×10^{-5} to 12.0×10^{-5} eq/g, and particularly preferably from 3.0×10^{-5} to 11.0×10^{-5} eq/g.

[0062] A method of adding the end-capping agent may be a method of feeding it together with raw materials such as caprolactam in the initial stage of polymerization, a method of adding it half way through polymerization, or a method of adding it when nylon resin in a molten state passes through a vertical stirring-type thin-film evaporator. The end-capping agent may be used as it is, or after having been dissolved in a small amount of solvent.

[0063] In the core-sheath conjugate fibers for artificial hair, in terms of making the touch and appearance of the fibers closer to those of human hair and further improving the curling property and curl retentive property, it is preferred that the core part comprises a polyester-based resin composition comprising at least one polyester resin selected from the group consisting of polyalkylene terephthalate and a copolymerized polyester comprising polyalkylene terephthalate as a main component, and it is more preferred that the sheath part comprises a polyamide-based resin composition comprising polyamide-based resin comprising at least one selected from the group consisting of nylon 6 and nylon 66 as a main component. In one embodiment of the present invention, "polyamide-based resin comprising at least one selected from the group consisting of nylon 6 and nylon 66 as a main component" refers to polyamide-based resin comprising nylon 6 and/or nylon 66 in an amount of 80 mol% or more.

[0064] The core-sheath conjugate fibers for artificial hair may comprise various additives as needed, such as a flame retardant other than the brominated epoxy-based flame retardant, a flame retardant auxiliary, a heat resistant agent, a stabilizer, a fluorescer, an antioxidant, an antistat and a pigment, as long as they do not interfere with the effects of the present invention.

[0065] The flame retardant other than the brominated epoxy-based flame retardant may be a phosphorus-containing flame retardant, a bromine-containing flame retardant, etc. Examples of the phosphorus-containing flame retardant include phosphate ester amide compounds and organic cyclic phosphorus-based compounds. Examples of the bromine-containing flame retardant include: pentabromotoluene; hexabromobenzene; decabromodiphenyl; decabromodiphenyl ether; bis(tribromophenoxy)ethane; tetrabromophthalic anhydride; ethylene bis(tetrabromophthalimide); ethylene bis(pentabromophenyl); octabromotrimethylphenylindan; bromine-containing phosphate esters such as tris(tribromoneopentyl)phosphate; brominated polystyrenes; brominated polybenzyl acrylates; brominated phenoxy resins; brominated polycarbonate oligomers; tetrabromobisphenol A and tetrabromobisphenol A derivatives such as tetrabromobisphenol A-bis(2,3-dibromopropyl ether), tetrabromobisphenol A-bis(allylether), and tetrabromobisphenol A-bis(hydroxyethyl ether); bromine-containing triazine-based compounds such as tris(tribromophenoxy)triazine; and bromine-containing isocyanuric acid compounds such as tris(2,3-dibromopropyl)isocyanurate. Particularly, the flame retardant other than the brominated epoxy-based flame retardant is preferably at least one selected from the group consisting of phosphate ester amide compounds, organic cyclic phosphorus-based compounds, and brominated phenoxy resin-based flame retardants because of their excellent flame resistance.

[0066] The flame retardant auxiliary may be an antimony-based compound, a composite metal comprising antimony, etc. Examples of the antimony-based compound include antimony trioxide, antimony tetroxide, antimony pentoxide, sodium antimonate, potassium antimonate, and calcium antimonate. In terms of an effect of improving flame resistance and touch, the flame retardant auxiliary is more preferably at least one selected from the group consisting of antimony

trioxide, antimony pentoxide, and sodium antimonate.

[0067] When the core-sheath conjugate fibers for artificial hair comprise a thermoplastic resin composition such as a polyester-based resin composition, the thermoplastic resin composition is melt kneaded using any of various general kneading machines to be formed into pellets, and the pellets are melt spun using a core-sheath type conjugate fiber spinneret to produce core-sheath conjugate fibers for artificial hair. For example, when the core-sheath conjugate fibers for artificial hair comprise a polyester-based resin composition, they can be produced by the following production method. A polyester-based resin composition obtained by dry-blending components including polyester resin and brominated epoxy-based flame retardant described above, is melt kneaded using any of various general kneading machines to be formed into pellets, and the pellets are melt spun to produce core-sheath conjugate fibers for artificial hair. The polyester-based resin composition may include other thermoplastic resins such as polycarbonate-based resin as needed. Further, when the core-sheath conjugate fibers for artificial hair comprise a polyamide-based resin composition, the polyamide-based resin composition is melt kneaded using any of various general kneading machines to be formed into pellets, and the pellets are melt spun to produce core-sheath conjugate fibers for artificial hair. Examples of the kneading machines include a single-screw extruder, a twin-screw extruder, a roll, a Banbury mixer, and a kneader. In particular, the twin-screw extruder is preferred in terms of adjusting the degree of kneading and simplifying operations.

[0068] As for the melt spinning, for example, the polyester-based resin composition is melt spun into yarns while the temperatures of an extruder, a gear pump, a spinneret, etc., are set at 250°C or more and 300°C or less. Then, spun yarns pass through a heated tube, cooled to a temperature of not more than the glass transition point of the polyester resin, and wound up at a speed of 50 m/min or more and 5000 m/min or less to obtain spun yarns (undrawn yarns). Further, for example, the polyamide-based resin composition is melt spun into yarns while the temperatures of an extruder, a gear pump, a spinneret, etc., are set at 260°C or more and 320°C or less. Then, spun yarns pass through a heated tube, cooled to a temperature of not more than the glass transition point of the polyamide resin, and wound up at a speed of 50 m/min or more and 5000 m/min or less to obtain spun yarns (undrawn yarns). In the melt spinning, the thermoplastic resin composition constituting the core part may be supplied by a core extruder, and the thermoplastic resin composition constituting the sheath part may be supplied by a sheath extruder.

[0069] Moreover, the spun yarns may be cooled in a water bath containing cooling water in order to control the fineness. The temperature and the length of the heated tube, the temperature and the amount of cooling air to be applied, the temperature of the cooling water bath, the cooling time, and the winding speed can be set appropriately in accordance with the extrusion rate of the polymer and the number of spinneret holes.

[0070] It is preferred that the spun yarns (undrawn yarns) are hot drawn. The drawing may be performed by either a two-step method or a direct spinning-drawing method. In the two-step method, the spun yarns are once wound, and then drawn. In the direct spinning-drawing method, the spun yarns are drawn continuously without winding. The hot drawing may be performed by a single-stage drawing method or a multi-stage drawing method including two or more stages.

[0071] The heating means in the hot drawing may be, e.g., a heating roller, a heat plate, a steam jet apparatus, or a hot water bath, and they can be used in combination appropriately.

[0072] Oils such as a fiber treatment agent and a softening agent may be applied to the core-sheath conjugate fibers for artificial hair to make the touch and feel of the fibers closer to the human hair. The fiber treatment agent may be, e.g., a silicone-based fiber treatment agent or a non-silicone-based fiber treatment agent for improving touch and combing property.

[0073] The single fiber fineness of the core-sheath conjugate fibers for artificial hair is preferably 10 dtex or more and 150 dtex or less, more preferably 30 dtex or more and 120 dtex or less, further preferably 40 dtex or more and 100 dtex or less, and particularly preferably 50 dtex or more and 90 dtex or less because the fineness within the above range is suitable for artificial hair.

[0074] The core-sheath conjugate fibers for artificial hair may be subjected to gear crimping. The gear crimping imparts gentle curves and natural appearance to fibers, and decreases cohesion between fibers, thereby improving the combing property. In the gear crimping, generally, fibers pass through two engaged gears while being heated to a temperature higher than its softening temperature to transfer the shape of the gears to the fibers, and thereby curves appear on the fibers.

[0075] The core-sheath conjugate fibers for artificial hair have latent crimpability, and express natural crimp by the heat treatment in the fiber processing stage, thereby having excellent curling property without the need for curl setting. Further, the core-sheath conjugate fibers for artificial hair have extremely favorable curl retentive property. Moreover, by heat-treating the core-sheath conjugate fibers for artificial hair at different temperatures in the fiber processing stage as needed, the fibers can express curls with different shapes.

[0076] The core-sheath conjugate fibers for artificial hair can be used for any hair ornament products. For example, the core-sheath conjugate fibers for artificial hair can be used for hair wigs, hairpieces, weavings, hair extensions, braided hair, hair accessories, and doll hair. Specifically, since the core-sheath conjugate fibers for artificial hair have latent crimpability and express natural crimp by the heat treatment in the fiber processing stage, hair ornament products

comprising the core-sheath conjugate fibers for artificial hair have excellent curling property without the need for curl setting. Further, the hair ornament products have extremely favorable curl retentive property. Moreover, by heat-treating the hair ornament products comprising the core-sheath conjugate fibers for artificial hair at different temperatures as needed, they can express curls with different shapes.

[0077] The above hair ornament products may comprise only the core-sheath conjugate fibers for artificial hair of the present invention, or a combination of the core-sheath conjugate fibers for artificial hair of the present invention and other artificial hair fibers, natural fibers such as human hair or animal hair, etc.

Examples

[0078] Hereinafter, the present invention will be described in more detail based on examples. However, the present invention is not limited to the examples.

[0079] The following are the measurement methods and evaluation methods applied in examples and comparative examples.

(Single Fiber Fineness)

[0080] The single fiber fineness was determined by averaging single fiber finenesses of 30 samples. The single fiber finenesses were measured using an auto-vibronic fineness measuring instrument "DENIER COMPUTER type DC-11" (manufactured by SEARCH CO., LTD.).

(Evaluation of Fiber Cross Section)

[0081] Fibers were bundled and fixed with a shrinkable tube to avoid displacement of the fiber bundle, and cut cross-sectionally with a cutter to prepare a fiber bundle for cross-sectional observation. The fiber bundle for cross-sectional observation was photographed at 400x magnification with a laser microscope ("VK-9500" manufactured by KEYENCE CORPORATION) to obtain fiber cross section micrographs. 30 fiber cross sections were selected randomly from the micrographs to measure the length of the major axis of the fiber cross section, the length of the first minor axis of the fiber cross section, the length of the second minor axis of the fiber cross section as well as the length of the major axis of the core part and the length of the first minor axis of the core part. In the core-sheath conjugate fibers for artificial hair in one embodiment of the present invention, the length of the major axis of the fiber cross section, the length of the first minor axis of the fiber cross section, the length of the second minor axis of the fiber cross section, the length of the major axis of the core part, the length of the first minor axis of the core part and the like can each be expressed by an average of the measured values of the 30 fiber cross sections selected randomly.

(Curling Property)

[0082] Fibers were cut into 63.5 cm long in a state where curls were stretched completely. 5.0 g of the 63.5 cm-long fibers obtained was bundled, and the length of the fiber bundle in a state where curls were stretched completely was adjusted to 70 cm by intentionally displacing the fibers using a hackling. Then, the fiber bundle was tied in the middle with a string, folded in two, and the string portion was fixed. The fiber bundle was fixed with an insulation lock at the position 30 cm away from the tip in a state where curls were stretched completely to prepare a fiber bundle for curling property evaluation. Next, the fiber bundle for curling property evaluation was hung perpendicular to the ground, and a length from the insulation lock, which fixed the upper end of the fiber bundle, to the lower end of the fiber bundle was measured (initial curl length). The curling property was determined under the following criteria based on the initial curl length and the curl strength.

A: The initial curl length is equivalent to the curl length of 100% human hair with cooling time of 0 second (fineness: 68 dtex, commercially available Chinese hair "Shake-N-Go Milky Way Pure Yaky Weave 100% Human Hair 14"-1B"), specifically, 25 cm or less. The curl strength is high, and the curl style is excellent.

B: The initial curl length is more than 25 cm and 29 cm or less. The curl strength from the upper part to the middle part of fibers is slightly weak, but the curl strength at the lower tip is strong, and the curl style is at an acceptable level.

C: The initial curl length exceeds 29 cm. The curl strength is weak as a whole, and the curl style is at an unsatisfactory level.

(Curl Retentivity)

[0083] The fiber bundle after evaluation of the curling property was fixed at its root and left to stand for three days

while being hung perpendicular to the ground. Three days later, the length from the insulation lock, which fixed the upper end of the fiber bundle, to the lower end of the fiber bundle was measured (curl length after three days), and a curl loosening percentage was calculated from the following formula. The curl retentivity of fibers was determined under the following criteria based on the curl length after three days and the curl shape. In the following formula for the curl loosening percentage, the initial curl length and the curl length after three days are both expressed in the unit "cm".

$$\text{Curl loosening percentage (\%)} = 100 - [(30 - \text{curl length after three days}) / (30 - \text{initial curl length})] \times 100$$

A: The curl loosening percentage is 0% or more and less than 5%, a change from the initial style is small, and curls as a whole remain spirally.

B: The curl loosening percentage is 5% or more and less than 10%, a change from the initial style is relatively small, and curls as a whole remain spirally.

C: The curl loosening percentage is 10% or more, curls as a whole become weak as compared with the initial style, and curls remain only at their tips.

(Touch)

[0084] Sensory evaluation was performed by a professional cosmetologist to determine touch under the following four criteria.

A: Very soft touch equivalent to human hair

B: Soft touch similar to human hair

C: Touch slightly harder than human hair

D: Touch harder than human hair

(Gloss)

[0085] 30 cm-long tow filaments having a total fineness of 100,000 dtex were visually observed by a professional cosmetologist under sunlight to evaluate the gloss under the following four criteria.

A: Gloss whose difference from the gloss of human hair cannot be recognized even when they are carefully compared with human hair

B: Gloss that can be judged to be higher or lower than the gloss of human hair when they are carefully compared with human hair

C: Gloss that can be judged to be higher or lower than the gloss of human hair when they are compared with human hair with normal attention

D: Gloss that can be judged to be apparently much higher or much lower than the gloss of human hair without the necessity of comparison

(Combing Property)

[0086] Fibers were cut into 63.5 cm long in a state where curls were stretched completely, and 5.0 g of the 63.5 cm-long fibers obtained was bundled. Then, the fiber bundle was tied in the middle with a string, folded in two, and the string portion was fixed to prepare a fiber bundle for hair ironing. Next, a hair iron ("IZUNAMI ITC450 Flat Iron" manufactured by Izunami Inc. (U.S.)) heated at 180°C was used to crimp the fiber bundle from the fixed root to the tip while heating. This process was repeated five times to prepare a fiber bundle for combing property evaluation. Thereafter, the fiber bundle for combing property evaluation was combed one hundred times from the fixed root to the tip using a hair comb ("MATADOR PROFESSIONAL 386.8 1/2F" made in Germany). The combing property was evaluated under the following criteria based on the number of deformed or split fibers.

A: The number of deformed or split fibers after one hundred times of combining is less than 10, and the fibers are combed through to the end with no resistance.

B: The number of deformed or split fibers after one hundred times of combining is 10 or more and less than 30, and the fibers are combed through to the end with slightly high resistance in the middle.

C: The number of deformed or split fibers after one hundred times of combining is 30 or more and less than 100,

the fibers are combed with high resistance in the middle, and the comb cannot pass through to the end with a probability of once to less than 20 times in 100 times.

D: The number of deformed or split fibers after one hundred times of combining is 100 or more, the fibers are combed with high resistance in the middle, and the comb cannot pass through to the end with a probability of 20 times or more in 100 times.

(Example 1)

[0087] Polyethylene terephthalate (trade name "BK-2180" manufactured by Mitsubishi Chemical Corporation) that had been dried to a moisture content of 100 ppm or less was supplied to a twin-screw extruder, melt kneaded at 280°C and formed into pellets. Nylon 66 (trade name "Zytel (registered trademark)-42A" manufactured by DuPont) that had been dried to a moisture content of 100 ppm or less was supplied to a twin-screw extruder, melt kneaded at 300°C and formed into pellets. The respective pellets were dried to a moisture content of 100 ppm or less. Then, the dried pellets were supplied to a melt spinning machine, and each molten polymer was extruded through a core-sheath type conjugate fiber spinneret with a nozzle shape indicated in Table 1 below at a barrel temperature of 280°C for polyethylene terephthalate and at a barrel temperature of 300°C for nylon 66. The extruded polymer was cooled to a temperature of not more than the glass transition temperature, and wound up at a speed of 60 to 150 m/min. Thus, undrawn yarns of eccentric core-sheath conjugate fibers comprising polyethylene terephthalate as the core part and nylon 66 as the sheath part and having a core-to-sheath area ratio (polyethylene terephthalate to nylon 66 area ratio) of core:sheath = 5:5 were obtained. The obtained undrawn yarns were drawn to 3 times at 80°C and heat-treated with a heating roller at 200°C. Finishing oil A (trade name "KWC-Q" manufactured by Marubishi Oil Chemical Corporation) and finishing oil B (trade name "KWC-B" manufactured by Marubishi Oil Chemical Corporation) were respectively applied thereto in amounts of 0.20% omf and 0.10% omf (weight percentage of finishing oil (pure content) relative to the dry fiber weight), followed by drying to obtain conjugate fibers (multifilaments) with a single fiber fineness indicated in Table 1 below. The single fiber fineness was measured as described above, and the same applied to the following.

(Example 2)

[0088] Conjugate fibers of Example 2 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the core-to-sheath area ratio was changed to core:sheath = 7:3.

(Example 3)

[0089] Conjugate fibers of Example 3 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the core-to-sheath area ratio was changed to core:sheath = 2:8.

(Example 4)

[0090] Conjugate fibers of Example 4 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the extrusion rate of the molten polymer during spinning was 1.3 times the extrusion rate of Example 1.

(Example 5)

[0091] Conjugate fibers of Example 5 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that: instead of nylon 66, polybutylene terephthalate (trade name "NOVADURAN (registered trademark) 5020" manufactured by Mitsubishi Engineering-Plastics Corporation) that had been dried to a moisture content of 100 ppm or less was supplied to a twin-screw extruder, melt kneaded at 260°C and formed into pellets; the molten polymer was extruded through a core-sheath type conjugate fiber spinneret with a nozzle shape indicated in Table 1 below at a barrel temperature of 260°C, and undrawn yarns of eccentric core-sheath conjugate fibers comprising polyethylene terephthalate as the core part and polybutylene terephthalate as the sheath part and having a core-to-sheath area ratio (polyethylene terephthalate to polybutylene terephthalate area ratio) of core:sheath = 5:5 were obtained.

(Comparative Example 1)

[0092] Conjugate fibers of Comparative Example 1 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the cross-sectional shape was changed to the shape indicated in Table 1 below.

(Comparative Example 2)

[0093] Conjugate fibers of Comparative Example 2 were attempted to be produced in the same manner as in Example 1 except that the cross-sectional shape was changed to the shape indicated in Table 1 below, and the spinneret was changed to a side-by-side type conjugate fiber spinneret. However, the two components were separated during drawing, and conjugate fibers could not be obtained.

(Comparative Example 3)

[0094] Conjugate fibers of Comparative Example 3 were attempted to be produced in the same manner as in Example 1 except that the core-to-sheath area ratio was changed to core:sheath = 8:2. However, the core part was exposed to the fiber surface, and favorable conjugate fibers could not be formed.

(Comparative Example 4)

[0095] Conjugate fibers of Comparative Example 4 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the core-to-sheath area ratio was changed to core:sheath = 1:9.

(Comparative Example 5)

[0096] Conjugate fibers (concentric core-sheath conjugate fibers) of Comparative Example 5 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the eccentricity was set to 0.0%.

(Comparative Example 6)

[0097] Polyamide-based fibers with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that: nylon 66 that had been dried to a moisture content of 100 ppm or less was supplied to a twin-screw extruder, melt kneaded at 300°C and formed into pellets; the pellets were dried to a moisture content of 100 ppm or less; and the dried pellets were supplied to a melt spinning machine, and the molten polymer was extruded through a spinneret with a nozzle shape indicated in Table 1 below at a barrel temperature of 300°C. The obtained fibers were cut into 63.5 cm long. 5.0 g of the 63.5 cm-long fibers obtained was bundled, and the length of the fiber bundle was adjusted to 70 cm by intentionally displacing the fibers using a hackling. Then, the fiber bundle was tied in the middle with a string, folded in two, and the string portion was fixed. The fiber bundle was fixed with an insulation lock at the position 30 cm away from the tip to prepare a fiber bundle for hair ironing. Next, a hair iron ("GOLD N HOT Professional Ceramic Spring Curling Iron 1-1/4 inch GH 2150" manufactured by Belson Products (U.S.)) heated at 180°C was used to hold the tip of the fiber bundle, wind the bundle up to the fixed root, and keep the state for three seconds. The fiber bundle was placed on a hand to keep the curl shape and released from the hand within one second. Thus, a curled fiber bundle was prepared.

(Comparative Example 7)

[0098] Conjugate fibers of Comparative Example 7 with a single fiber fineness indicated in Table 1 below were obtained in the same manner as in Example 1 except that the cross-sectional shape was changed to the shape indicated in Table 1 below, and the eccentricity was set to 0.0%.

[0099] The fiber cross sections of the fibers of examples and comparative examples were evaluated by the evaluation methods described above, and the results are shown in Table 1 below. The touch, appearance, curling property, curl retentivity, and combing property of the fibers of examples and comparative examples were evaluated by the evaluation methods described above, and the results are shown in Table 1 below. FIGS. 5 to 8 are laser micrographs (400x magnification) of the fiber cross sections of the fibers of Example 3 and Comparative Examples 1, 5, and 6.

[Table 1]

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Fiber shape	Flat two- lobe	Flat two- lobe	Flat two- lobe	Flat two- lobe	Flat two- lobe	Round	Flat two- lobe (side- by-side)	Flat two- lobe	Flat two- lobe	Flat two- lobe	Flat two- lobe	Round
Core part shape	Ellipse	Ellipse	Ellipse	Ellipse	Ellipse	Round		Ellipse	Ellipse	Ellipse	-	Round
Core-to-sheath area ratio	5:5	7:3	2:8	5:5	5:5	5:5	5:5	8:2	1:9	5:5	-	5:5
Eccentricity (%)	23.0	16.3	25.0	14.7	20.8	15.8	-	-	27.9	0.0	-	0.0
Single fiber fineness (dtex)	68.7	71.7	64.3	92.0	58.7	66.7	-	-	57.0	62.0	62.5	65.1
Fiber cross section micrograph	-	-	FIG. 5	-	-	FIG. 6	-	-	-	FIG. 7	FIG. 8	-
Fiber cross section	Length L of major axis (μm)	91.5	99.4	102.3	92.0	83.3	-	-	100.6	101.6	96.3	80.8
	Length S1 of first minor axis (μm)	71.8	67.4	70.9	81.6	61.7	-	-	71.4	65.3	68.6	79.7
	Length S2 of second minor axis (μm)	67.0	64.2	66.6	72.7	58.7	-	-	67.5	63.9	66.1	79.7
	Ratio of major axis to first minor axis	1.39	1.36	1.40	1.25	1.49	-	-	1.41	1.56	1.40	1.01
	Ratio of second minor axis to first minor axis	0.93	0.95	0.94	0.89	0.95	-	-	0.95	0.98	0.96	1.00

(continued)

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Core part	Length Lc of major axis (μm)											
	71.9	73.9	52.7	78.3	64.3	57.9	-	-	43.1	71.4	-	57.6
	Length Sc of first minor axis (μm)											
Ratio of major axis to first minor axis	53.2	57.6	40.6	57.2	54.2	57.6	-	-	34.7	46.3	-	57.4
	Ratio of major axis to first minor axis											
	1.35	1.28	1.30	1.37	1.19	1.01	-	-	1.24	1.54	-	1.00
Curling property	Initial curl length (cm)											
	24.0	29.0	28.0	20.5	28.4	30.0	-	-	29.6	30.0	27.2	30.0
Curl retentivity	Judgement											
	A	B	B	A	B	C	-	-	C	C	B	C
Appearance	Curl loosening percentage (%)											
	0	0	0	2.4	1.8	-	-	-	-	-	16.3	-
Quality of Fibers	Judgement											
	A	A	A	A	A	-	-	-	-	-	C	-
Combining property	Gloss											
	B	B	B	B	B	C	-	-	B	B	B	C
Quality of Fibers	Touch											
	A	B	A	A	B	B	-	-	A	A	A	B
Quality of Fibers	Combining property											
	A	A	A	A	A	D	-	-	A	A	A	D
*Ex.: Example, Comp. Ex.: Comparative Example												

[0100] As can be seen from the results of Table 1 above, the fibers of Examples 1 to 5 had curls by latent crimpability while having touch and appearance (gloss) similar to human hair, thereby exhibiting excellent curling property without the need for curl setting, having extremely high curl retentive property, and having favorable appearance, touch and combing property. Meanwhile, the fibers of Comparative Example 1 and Comparative Example 7 having a circular cross section did not exhibit crimpability, and they were inferior in appearance and combing property. The fibers of Comparative Example 2 having a simple side-by-side structure resulted in the separation of the two components, so that conjugate fibers could not be obtained. The fibers of Comparative Example 3 resulted in the exposure of the core part to the fiber surface, so that they could not be molded as favorable conjugate fibers. The fibers of Comparative Example 4 and Comparative Example 5 were poor in crimpability, and curling property could not be observed. The fibers of Comparative Example 6 exhibited favorable curling property directly after being curled with a hair iron, but they were very poor in curl retentivity.

Description of Reference Numerals

[0101]

- 1 Core-sheath conjugate fiber for artificial hair (cross section)
- 10 Sheath part
- 11 Central point of the major axis of the fiber cross section
- 12 Major axis of the fiber cross section
- 13 First minor axis of the fiber cross section
- 14 Second minor axis of the fiber cross section
- 20 Core part
- 21 Central point of the major axis of the core part
- 22 Major axis of the core part
- 23 First minor axis of the core part

Claims

1. A core-sheath conjugate fiber for artificial hair comprising a core part and a sheath part, wherein the core-sheath conjugate fiber for artificial hair has a core-to-sheath area ratio of core:sheath = 2:8 to 7:3 and an eccentricity of 5% or more, the core-sheath conjugate fiber for artificial hair has a flat multilobed shape in cross section, in the fiber cross section, a ratio of a length of a major axis of the fiber cross section to a length of a first minor axis of the fiber cross section is 1.10 or more and 3.00 or less, where the major axis of the fiber cross section is a longest straight line among a symmetrical axis of the fiber cross section and straight lines that connect any two points on an outer circumference of the fiber cross section and that extend parallel to the symmetrical axis of the fiber cross section, and the first minor axis of the fiber cross section is a longest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section, in the fiber cross section, a ratio of a length of a major axis of the core part to a length of a first minor axis of the core part is 1.10 or more and 3.00 or less, where the major axis of the core part is a longest straight line among a symmetrical axis of the core part and straight lines that connect any two points on an outer circumference of the core part and that extend parallel to the symmetrical axis of the core part, and the first minor axis of the core part is a longest straight line formed when any two points on the outer circumference of the core part are connected perpendicular to the major axis of the core part, and a direction of the major axis of the fiber cross section and a direction of the major axis of the core part substantially coincide with each other.
2. The core-sheath conjugate fiber for artificial hair according to claim 1, wherein in the fiber cross section, a ratio of a length of a second minor axis of the fiber cross section to the length of the first minor axis of the fiber cross section is 0.50 or more and less than 1.00, where the second minor axis of the fiber cross section is a shortest straight line formed when any two points on the outer circumference of the fiber cross section are connected perpendicular to the major axis of the fiber cross section.
3. The core-sheath conjugate fiber for artificial hair according to claim 1 or 2, wherein the flat multilobed shape is a flat two-lobed shape in which two circles, two ellipses, or one circle and one ellipse are connected via recesses.

4. The core-sheath conjugate fiber for artificial hair according to any one of claims 1 to 3, wherein the core-sheath conjugate fiber for artificial hair comprises at least one resin composition selected from the group consisting of a polyester-based resin composition, a polyamide-based resin composition, a vinyl chloride-based resin composition, a modacrylic-based resin composition, a polycarbonate-based resin composition, a polyolefin-based resin composition, and a polyphenylene sulfide-based resin composition.
5. The core-sheath conjugate fiber for artificial hair according to any one of claims 1 to 4, wherein the core part and/or sheath part of the core-sheath conjugate fiber for artificial hair comprises a polyester-based resin composition comprising at least one polyester-based resin selected from the group consisting of polyalkylene terephthalate and a copolymerized polyester comprising polyalkylene terephthalate as a main component.
6. The core-sheath conjugate fiber for artificial hair according to any one of claims 1 to 5, wherein the core part and/or sheath part of the core-sheath conjugate fiber for artificial hair comprises a polyamide-based resin composition comprising polyamide-based resin comprising at least one selected from the group consisting of nylon 6 and nylon 66 as a main component.
7. A hair ornament product comprising the core-sheath conjugate fiber for artificial hair according to any one of claims 1 to 6.
8. The hair ornament product according to claim 7, wherein the hair ornament product is any one selected from the group consisting of a hair wig, a hairpiece, weaving hair, a hair extension, braided hair, a hair accessory, and doll hair.

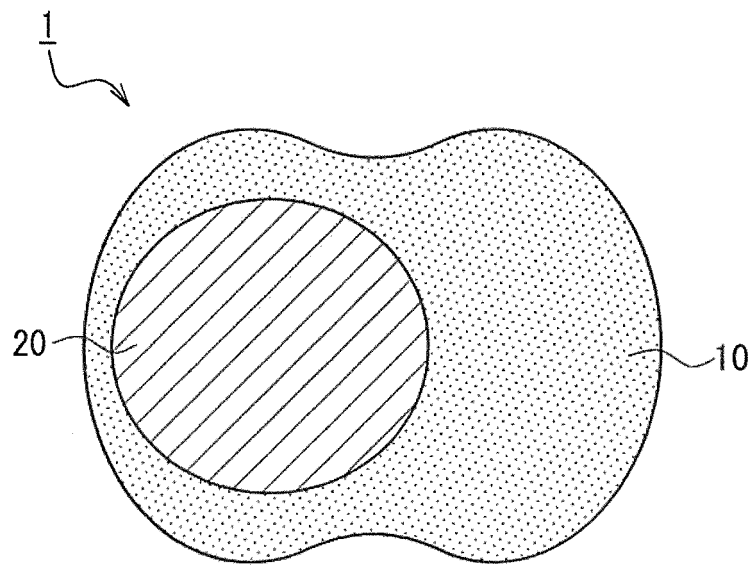


FIG. 1

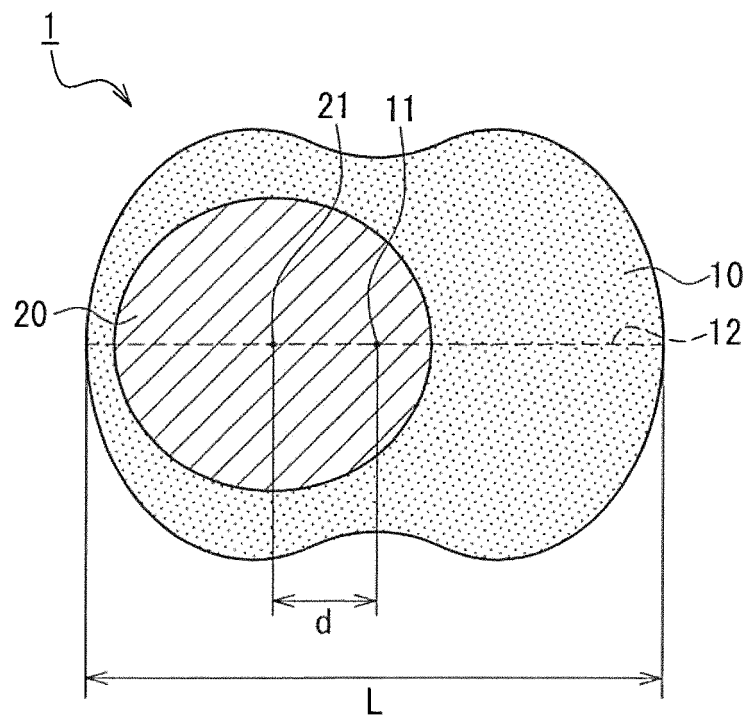


FIG. 2

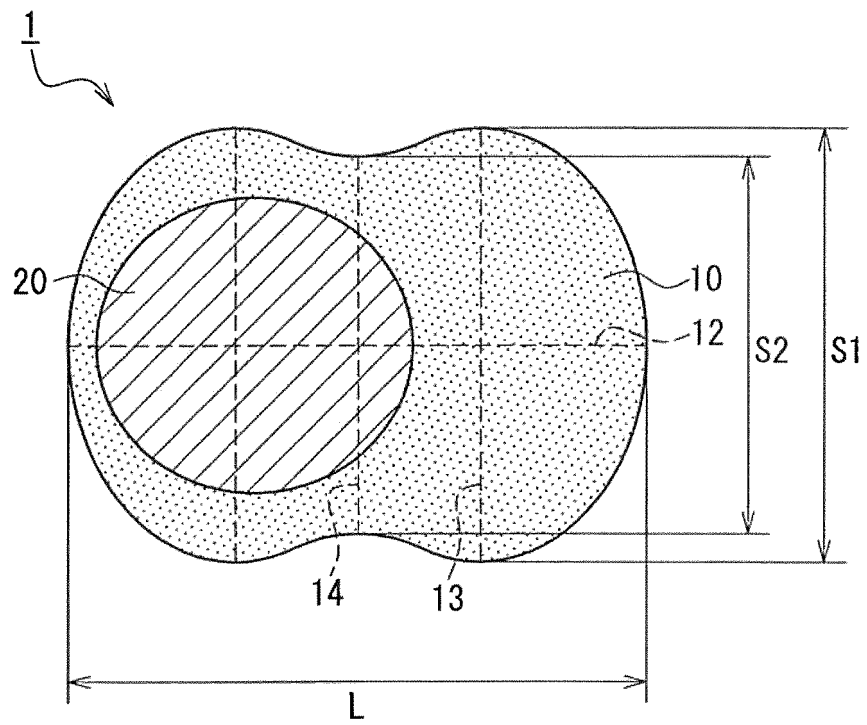


FIG. 3

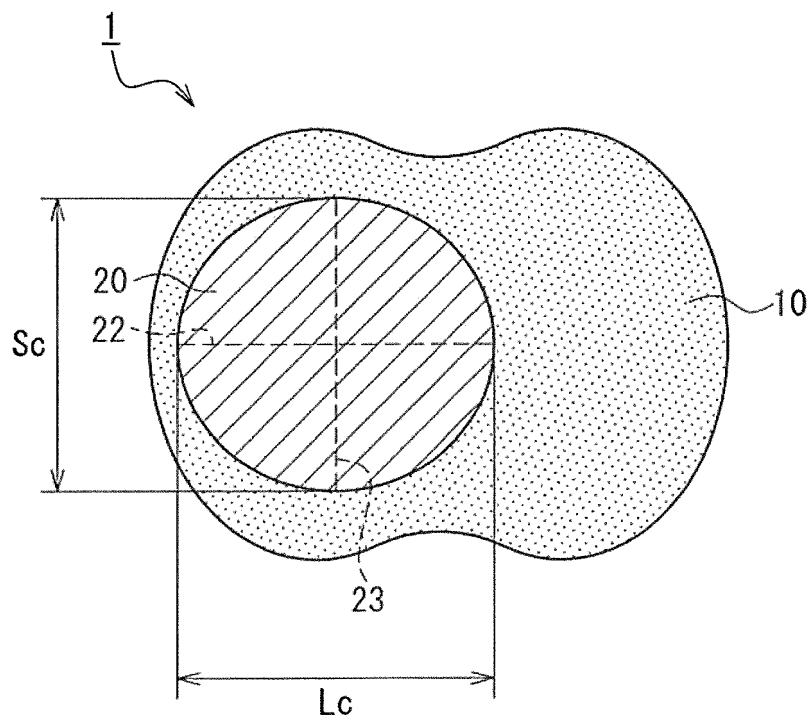


FIG. 4

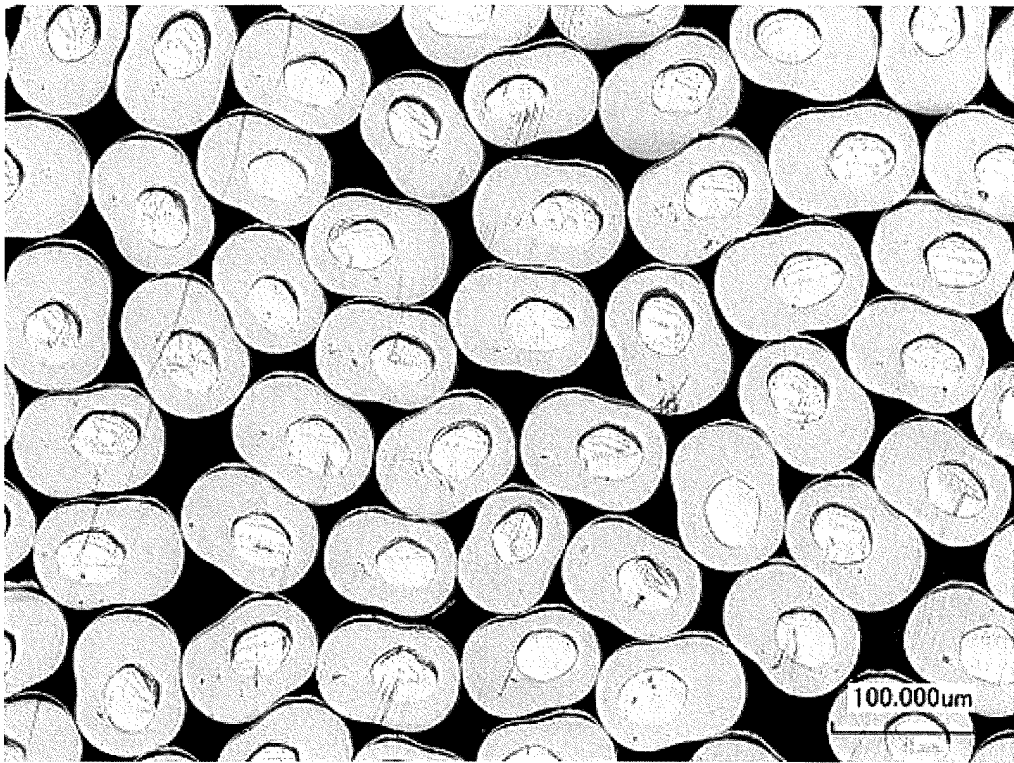


FIG. 5



FIG. 6



FIG. 7



FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/003154

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. A41G3/00 (2006.01) i, D01F8/14 (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. A41G3/00, D01F8/14

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.
Y	JP 49-12312 B1 (KANEBO LIMITED) 23 March 1974, column 2, line 18 to column 3, line 15, column 4, lines 13-28, column 6, lines 23, 24, column 7, line 2 to column 8, line 2, fig. 3 (Family: none)	1-8
Y	JP 45-36854 B1 (TORAY INDUSTRIES) 24 November 1970, column 1, line 21 to column 5, line 13, table 1, fig. 1, 2 (Family: none)	1-8

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

* Special categories of cited documents:

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Date of the actual completion of the international search
28.03.2018Date of mailing of the international search report
10.04.2018Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/003154

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 61-49402 B2 (PAPAGEORGIOU, D. G.) 29 October 1986, column 3, line 14 to column 10, line 12, fig. 1-11 & US 4302491 A, column 1, line 1 to column 6, line 27, fig. 1-11 & EP 0001990 A1	1-8
Y	JP 10-168647 A (KANEKA CORPORATION) 23 June 1998, paragraphs [0001]-[0006], table 1, fig. 25 (Family: none)	1-8
Y	JP 2006-316395 A (KANEKA CORPORATION) 24 November 2006, paragraphs [0008]-[0010], [0049], [0050], table 1, fig. 1 (Family: none)	1-8
Y	Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 56008/1971 (Laid-open No. 13277/1973) (KURARAY CO., LTD.) 14 February 1973, specification, page 1, line 14 to page 3, line 14, fig. 1 (Family: none)	1-8
A	JP 6034966 B2 (KANEKA CORPORATION) 30 November 2016, paragraphs [0005]-[0010], [0062], table 1, fig. 1, 2, 5, 6 & US 2016/0088888 A1, paragraphs [0006]-[0011], [0076]-[0082], table 1, fig. 1, 2, 5-6C & WO 2014/196642 A1 & CN 105263348 A & KR 10-2016-0006260 A	1-8
A	JP 2006-241665 A (TOWERFIELD ENTERPRISES LTD.) 14 September 2006, paragraphs [0008]-[0010], [0015], fig. 4 & US 2006/0194050 A1, paragraphs [0013]-[0015], [0019], fig. 4 & EP 1696072 A1 & CN 1823642 A	1-8

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2006087911 A [0006]
- JP 2002129432 A [0006]