POLYPHENYLENE SULFIDE COMPOSITE FIBER AND NONWOVEN FABRIC

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ABSTRACT

Provided are a composite fiber which consists primarily of resins comprising polyphenylene sulfide as their main constituents and which has both thermal dimensional stability and excellent thermal bondability, and a nonwoven fabric. The composite fiber consists primarily of component A and component B, the component A being a resin that includes polyphenylene sulfide as its main constituent, the component B being a resin that includes polyphenylene sulfide as its main constituent, having a higher melt flow rate than the component A, and forming at least part of the surface of the fiber.
POLYPHENYLENE SULFIDE COMPOSITE FIBER AND NONWOVEN FABRIC

FIELD OF THE INVENTION

The present invention relates to a polyphenylene sulfide (sometimes abbreviated as "PPS") composite fiber which consists primarily of resins comprising PPS as their main constituents and which is excellent in heat resistance and chemical resistance, and to a nonwoven fabric made from the fiber.

BACKGROUND OF THE INVENTION

A PPS resin has excellent characteristics such as heat resistance, flame retardancy and chemical resistance, and is suitable for engineering plastics, films, fibers, nonwoven fabrics, and the like. In particular, nonwoven fabrics utilizing these excellent characteristics are expected to be used for industrial applications such as heat-resistant filters, electrical insulating materials and battery separators.

There has been proposed, as a nonwoven fabric made from a PPS resin, a long-fiber nonwoven fabric produced by spinning a PPS resin and drawing the resulting long fibers to form fabric by spunbonding, temporarily bonding the fabric at a temperature not higher than the first crystallization temperature of the fabric, heat treating the fabric under tension at a temperature not lower than the first crystallization temperature, and thermal bonding the fabric (see Patent Literature 1). However, in such a process with heat treatment, the crystallinity of the fibers becomes too high, which leads to insufficient thermal bondability resulting in a nonwoven fabric of a low mechanical strength.

Another proposed nonwoven fabric is a heat-resistant nonwoven fabric produced by spinning fibers comprising 30 wt% or more of a PPS fiber with a degree of crystallinity of 25 to 50% at a spinning rate of 6000 m/min or more, and integrating the fibers by thermal bonding (see Patent Literature 2). However, the fibers produced by high-speed spinning at a spinning rate of 6000 m/min or more have a high crystallinity, which leads to insufficient thermal bondability resulting in a nonwoven fabric of a low mechanical strength.

In general, higher crystallinity of synthetic fibers results in higher thermal dimensional stability and a lower thermal bondability. In other words, thermal dimensional stability and thermal bondability are in a trade-off relationship. In particular, in the case of PPS fibers, achieving both qualities at the same time is difficult as described above.

In order to solve this problem, the applicants of the present invention have proposed a PPS long-fiber nonwoven fabric having both thermal dimensional stability and excellent thermal bondability, in particular, a long-fiber nonwoven fabric produced by drawing and stretching long fibers by hot compressed air and thermally bonding the resulting web (see Patent Literature 3).

Indeed, this technique was able to achieve a certain effect of imparting thermal dimensional stability and improving thermal bondability, but when the mass per unit area was high, sufficient thermal bondability could not be obtained.

Thus, there has been provided a PPS fiber having both thermal dimensional stability and excellent thermal bondability or a PPS nonwoven fabric having a high mechanical strength.

PATENT LITERATURE

Patent Literature 1: JP 2008-223209 A

SUMMARY OF THE INVENTION

An object of the present invention is to provide a polyphenylene sulfide composite fiber having both thermal dimensional stability and excellent thermal bondability and a nonwoven fabric being made from the fiber and having a high mechanical strength.

That is, the present invention includes, according to an aspect of the invention, a polyphenylene sulfide composite fiber consisting primarily of component A and component B, component A being a resin that comprises polyphenylene sulfide as its main constituent, component B being a resin that comprises polyphenylene sulfide as its main constituent, having a higher melt flow rate (hereinafter, melt flow rate is also referred to as MFR) than component A, and forming at least part of the surface of the fiber.

The present invention also includes a nonwoven fabric made from the polyphenylene sulfide composite fiber.

The PPS composite fiber of the present invention has both thermal dimensional stability and excellent thermal bondability. Hence, the nonwoven fabric of the present invention has both thermal dimensional stability and excellent mechanical strength, and therefore can be used for various industrial applications.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

An important feature of the composite fiber of embodiments of the present invention is that the fiber consists primarily of component A and component B and that each of the components comprises PPS as its main constituent. With this configuration, the fiber exhibits excellent heat resistance, flame retardancy and chemical resistance. The term "consists primarily of" means that the components account for 90% by mass or more of the total mass of the fiber. The term "comprises as its main constituent" means that a particular ingredient accounts for 85% by mass or more of the total mass of the fiber, component, or the fiber.

Another important feature of the PPS composite fiber of embodiments of the present invention is that it is a PPS composite fiber consisting primarily of component A and component B, component A being a resin that comprises polyphenylene sulfide as its main constituent, component B being a resin that comprises polyphenylene sulfide as its main constituent, having a higher melt flow rate than component A, and forming at least part of the surface of the fiber.

In general, fibers produced by a common spinning process have fiber structure in which orientation and crystallinity are increased from the center of the cross section of the fiber to the surface of the fiber. This structure is created as follows: cooling of fibers spun from a spinneret proceeds from the fiber surface toward the inside of the fibers, and due to the cooling, the fluidity of the fiber surface is reduced, causing the concentration of spinning stress on the fiber surface, and then oriented crystallization proceeds therefrom.

With such fiber structure, even when the fiber as a whole has a low crystallinity, the fiber surface, which is cru-
cially important for thermal bonding, has a high crystallinity, resulting in insufficient thermal bondability.

[0021] The present invention includes a composite fiber consisting primarily of component A and component B, component A being a resin that comprises polyphenylene sulfide as its main constituent, component B being a resin that comprises polyethylene sulfide as its main constituent and having a higher melt flow rate than component A. In this composite fiber, spinning stress is concentrated on component A, and thereby the orientation and crystallization of component B is suppressed. Further, at least part of the fiber surface is formed of component B with suppressed orientation and crystallinity, and as a result the fiber has thermal dimensional stability and very excellent thermal bondability.

[0022] As described above, the fiber comprising polyphenylene sulfide as its main constituent has a lower crystallinity in at least part of the fiber surface than in the center of the cross section of the fiber when the crystallinity of the fiber surface is measured in the region from the fiber surface to 1 μm in radially inward direction of the fiber. The fiber provided with such fiber structure with the opposite configuration to that of the structure of fibers produced by common spinning process achieves both thermal dimensional stability and very excellent thermal bondability.

[0023] The PPS in components A and B preferably contains 93 mol% or more of p-phenylene sulfide units. The PPS containing 93 mol% or more of p-phenylene sulfide units, more preferably 95 mol% or more of p-phenylene sulfide units, provides excellent spinnability and produces fibers with excellent mechanical strength.

[0024] Components A and B each preferably contain 85% by mass or more of the PPS resin, more preferably 90% by mass or more of the PPS resin, further more preferably 95% by mass or more of the PPS resin, for achieving heat resistance, chemical resistance, and the like.

[0025] Components A and B each may contain a thermoplastic resin other than the PPS resin as long as the effects of the present invention are not impaired. Examples of the thermoplastic resin other than the PPS resin include polyetherimide, polyethersulfone, polysulfone, polyphenylene ether, polyether, polyarylute, polyamide, polyamide-imide, polycarbonate, polyolefin, and polyether ether ketone.

[0026] Components A and B each may contain additives such as nucleating agents, delustrants, pigments, antifungal agents, antimicrobial agents, fire retardants and hydrophilizing agents, as long as the effects of the present invention are not impaired.

[0027] The MFR of component A of the present invention as measured in accordance with ASTM D1238-70 (measurement temperature: 315.5°C., applied load: 5 kg) is preferably 50 to 300 g/10 min. When the MFR is 50 g/10 min or more, more preferably 100 g/10 min or more, adequate fluidity is obtained, and thereby an increase in the back pressure at the spinneret is suppressed and breakage of fibers during drawing and stretching is prevented. When the MFR is 300 g/10 min or less, more preferably 225 g/10 min or less, an appropriately high polymerization degree or molecular weight is obtained, and thereby sufficient mechanical strength and heat resistance for practical use are obtained.

[0028] Another important feature of embodiments of the present invention is that the MFR (as measured in accordance with the above ASTM D1238-70) of component B of the present invention is higher (i.e., the viscosity is lower) than that of component A. The difference obtained by subtracting the MFR of component A from the MFR of component B is preferably 10 g/10 min or more, more preferably 50 g/10 min or more, further more preferably 100 g/10 min or more. With this condition, spinning stress imposed to component B is reduced, and thereby the oriented crystallization of component B is suppressed.

[0029] The difference obtained by subtracting the MFR of component A from the MFR of component B is preferably 1000 g/10 min or less, more preferably 500 g/10 min or less, further more preferably 200 g/10 min or less. With this condition, adequate fluidity is obtained, and thereby stable spinning can be performed.

[0030] The amount of component B is preferably 5 to 70% by mass of the total amount of the PPS composite fiber. When the amount of component B is 5% by mass or more, more preferably 10% by mass or more, furthermore preferably 15% by mass or more, strong thermal bonding is achieved efficiently. When the amount of component B is 70% by mass or less, more preferably 50% by mass or less, further more preferably 30% by mass or less, the decrease in mechanical strength is prevented.

[0031] An important feature of the composite form of the PPS composite fiber of embodiments of the present invention is that component B forms at least part of the fiber surface. The advantage of this configuration is that component B exposed to the surface of the fiber contributes to thermal bonding. In addition, component A is preferably successively disposed in the longitudinal direction of the PPS composite fiber of the present invention. The successive disposition of component A in the longitudinal direction of the fiber more effectively concentrates spinning stress on component A and suppresses the orientation and crystallization of component B.

[0032] Examples of the composite form of the PPS composite fiber of the present invention include a core-shell type of which the cross section has circle-shaped component A surrounded by concentric donut-shaped component B, an eccentric core-shell type in which the center of component A is not coaxial with the center of component B, an islands-in-the-sea type containing component A as the sea component and component B as the island component, a side-by-side type containing components A and B lying side-by-side, a segmented pie type in which components A and B are alternately arranged in radial segments, and a multilobate type containing several portions of component B arranged around component A. Among them, preferred is the core-shell type in which the component B occupies the entire surface of the fiber and which is excellent in spinnability.

[0033] The average single fiber fineness of the PPS composite fiber of the present invention is preferably 0.5 to 10 dtex. When the average single fiber fineness is 0.5 dtex or more, more preferably 1 dtex or more, further more preferably 2 dtex or more, the spinnability of the fiber is maintained and frequent breakage of the fiber during spinning is prevented. When the average single fiber fineness is 10 dtex or less, more preferably 5 dtex or less, further more preferably 4 dtex or less, the amount of the extruded molten resin per spinneret hole is appropriately reduced so that the spun fibers are sufficiently cooled, thereby preventing the deterioration of spinnability caused by fusion of the fibers. In addition, the fiber with such average single fiber fineness can produce a nonwoven fabric not having varying mass per unit area but having excellent quality of the surface. Considering the dust-collecting performance of the nonwoven fabric in use as a filter or the like, the average single fiber fineness is preferably 10 dtex or less, more preferably 5 dtex or less, and further more preferably 4 dtex or less.

[0034] The PPS composite fiber of the present invention can be produced as a multifilament yarn, a monofilament yarn or a staple yarn, and can also be used to produce any types of
fabrics such as woven fabrics and nonwoven fabrics. The PPS composite fiber of the present invention is especially preferably used to produce a nonwoven fabric. This is because, in a nonwoven fabric, the PPS composite fibers thermally bonded to each other and thereby enhance the strength of the nonwoven fabric.

Examples of the nonwoven fabrics include needle punched nonwoven fabrics, wet-laid nonwoven fabrics, spunlace nonwoven fabrics, spunbonded nonwoven fabrics, meltblown nonwoven fabrics, resin-bonded nonwoven fabrics, chemical-bonded nonwoven fabrics, thermally bonded nonwoven fabrics, tow-opening nonwoven fabrics, and air-laid nonwoven fabrics. Among them, preferred are spunbonded nonwoven fabrics, which are excellent in productivity and mechanical strength.

The nonwoven fabric made from the PPS composite fiber of the present invention exhibits a high mechanical strength after thermal bonding, and therefore the nonwoven fabric of the present invention is preferably produced by integrating the fibers by thermal bonding.

The mass per unit area of the nonwoven fabric of the present invention is preferably 10 to 1,000 g/m². When the mass per unit area of the nonwoven fabric of the present invention is 10 g/m² or more, preferably 100 g/m² or more, further preferably 200 g/m² or more, the nonwoven fabric exhibits sufficient mechanical strength for practical use. When the mass per unit area of the nonwoven fabric of the present invention is 1,000 g/m² or less, preferably 700 g/m² or less, further preferably 500 g/m² or less, the nonwoven fabric exhibits adequate breathability and thereby will not cause high pressure drop when used as a filter or the like.

From the tensile strength in the longitudinal direction, the tensile elongation in the longitudinal direction and the mass per unit area of the nonwoven fabric, the product of strength and elongation per mass per unit area is calculated by the formula below. The product of strength and elongation per mass per unit area of the nonwoven fabric made from the thermally bondable composite fiber of the present invention is preferably 25 or more.

Product of strength and elongation per mass per unit area = longitudinal tensile strength (N/5 cm) × longitudinal tensile elongation (%/mass per unit area (g/m²))

When the product of strength and elongation per mass per unit area is 25 or more, preferably 35 or more, further preferably 40 or more, the nonwoven fabric has sufficient mechanical strength for use in severe environment. The upper limit of the product of strength and elongation per mass per unit area is not particularly defined, but the product of strength and elongation per mass per unit area of the nonwoven fabric of the present invention is preferably 100 or less so that the nonwoven fabric is not too hard to handle.

Preferred embodiments of processes for producing the PPS composite fiber and the nonwoven fabric of the present invention will be described below.

The PPS composite fiber of the present invention can be produced by a conventional melt spinning process. For example, for the production of a core-sheath composite fiber, a PPS resin as the core component and a PPS resin as the sheath component are melted in separate extruders, metered, fed to a spinneret for core-sheath composite spinning, and melt spun into continuous fibers. The fibers are cooled with a conventional cooling device that blows air laterally or circularly, in air is applied to the fibers, and the fibers are taken up on a winder with a take-up roller to produce a core-sheath composite fiber as undrawn fibers. When the composite fiber is desired to be provided in the form of short fibers, the wound undrawn fibers are drawn with a conventional drawing machine having a plurality of pairs of rollers at different circumferential speeds, crimped in a stuffer-box crimper or the like, and cut into a desired length with a cutter such as an FC cutter. When the composite fiber is desired to be provided in the form of long fibers, the wound undrawn fibers are drawn with a drawing machine, taken up, and, if necessary, subjected to processing such as twisting and false twisting.

A process for producing a composite-fiber nonwoven fabric by spinning process, which is a preferred embodiment of the nonwoven fabric of the present invention, will be described below.

Spunbonding process is a production process involving melting a resin, spinning continuous fibers from the molten resin by extruding it from a spinneret, cooling and solidifying the fibers, drawing and stretching the fibers with an ejector, collecting the fibers on a moving net to form a nonwoven web, and thermally bonding the web.

The spinneret and the ejector may be in various shapes such as a circular shape and a rectangular shape. Inter alia, a combination of a rectangular spinneret and a rectangular ejector is preferred so that the amount of compressed air to be used is relatively small and the continuous fibers hardly fuse to each other or rub against each other.

The spinning temperature for melting and spinning the resin is preferably 290 to 380°C, more preferably 295 to 360°C, further preferably 300 to 340°C. The spinning temperature within the above range allows the resin to be in a stable molten state and to exhibit excellent spinning stability.

Components A and B are melted in separate extruders, metered, and fed to a spinneret for composite spinning, and spun into composite fibers.

Cooling of the spun continuous composite fibers may be performed by, for example, a method in which cold air is forced to blow over the continuous fibers, a method in which the continuous fibers are allowed to cool down at ambient temperature around the fibers, a method in which the distance between the spinneret and the ejector is adjusted, or a combined method thereof. Cooling conditions can be appropriately adjusted based on the discharge rate per spinneret hole, the spinning temperature, the ambient temperature, and the like.

The continuous fibers solidified by cooling are drawn and stretched by compressed air ejected from the ejector. The methods and conditions for drawing and stretching the fibers by means of the ejector are not particularly limited, but preferred are methods that efficiently promote the crystallization of the PPS fibers, in particular, a method in which the fibers are drawn and stretched at a spinning rate of 3,000 m/min or more by compressed air that is heated to 100°C or higher and then ejected from the ejector, or a method in which the fibers are drawn and stretched at a spinning rate of not less than 5,000 m/min and less than 6,000 m/min by compressed air (at normal temperature) ejected from the ejector that is disposed so that the compressed air outlet of the ejector is 450 to 650 mm distant from the bottom of the spinneret.

The drawn PPS composite fibers are collected on a moving net to form a nonwoven web, and the obtained nonwoven web is integrated by thermal bonding to form a nonwoven fabric.

The thermal bonding can be performed by, for example, thermal pressure bonding using various types of rolls, such as a hot embossing roll pair of upper and lower rolls each having an embossed surface, a hot embossing roll pair of a roll having a flat (smooth) surface and a roll having an embossed surface, and a hot calendaring roll pair of upper and lower flat (smooth) rolls; and through-air bonding involv-
ing passing hot air through a nonwoven web in the thickness direction thereof. Among these, preferred is thermal bonding using a hot embossing roll pair, which improves the mechanical strength and allows the nonwoven fabric to retain adequate breathability.

[0052] The emboss pattern on the embossing roll(s) may be circle, oval, square, rectangle, parallelogram, diamond, regular hexagon, regular octagon, or the like.

[0053] Regarding the surface temperature of the hot embossing roll pair, since the PPS composite fiber of the present invention is very excellent in thermal bondability and thus can be thermally bonded at a lower temperature than usual, the surface temperature of the hot embossing roll pair is preferably 150 to 5°C lower than the melting point of PPS. When the surface temperature of the hot embossing roll pair is not lower than the temperature that is 150°C lower than the melting point of PPS, more preferably not lower than the temperature that is 100°C lower than the melting point of PPS, further more preferably not lower than the temperature that is 50°C lower than the melting point of PPS, the fibers are sufficiently thermally bonded and thereby flaking off and fluffing of the resulting nonwoven fabric are prevented. When the surface temperature of the hot embossing roll pair is not higher than the temperature that is 5°C lower than the melting point of PPS, holes in the press-bonded parts due to melting of the fibers are prevented from being generated.

[0054] The linear pressure applied by the hot embossing roll pair during thermal bonding is preferably 200 to 1500 N/cm. When the linear pressure applied by the hot embossing roll pair is 200 N/cm or more, more preferably 300 N/cm or more, the fibers are sufficiently thermally bonded and thereby flaking off and fluffing of the resulting sheet is prevented. When the linear pressure applied by the hot embossing roll pair is 1500 N/cm or less, more preferably 1000 N/cm or less, the raised portions of the embossing roll(s) are prevented from biting into the nonwoven fabric and thereby difficulty in removing the nonwoven fabric from the roll(s) and the breakage of the nonwoven fabric are prevented.

[0055] The bonded area formed by the hot embossing roll pair is preferably 8 to 40%. When the bonded area is 8% or more, more preferably 10% or more, further more preferably 12% or more, the resulting nonwoven fabric will have sufficient strength for practical use. When the bonded area is 40% or less, more preferably 30% or less, further more preferably 20% or less, the resulting nonwoven fabric is prevented from being formed into a film-like fabric that hardly exhibits the advantages of a nonwoven fabric, such as breathability. In cases where the thermal bonding is performed with a pair of upper and lower rolls each having raised and recessed portions, the term “bonded area” herein refers to the ratio of the area of the nonwoven web in contact with both of the raised portions of the upper roll and the raised portions of the lower roll, relative to the total area of the nonwoven web. In cases where the thermal bonding is performed with a pair of a roll having raised and recessed portions and a flat roll, the term “bonded area” herein refers to the ratio of the area of the nonwoven web in contact with the raised portions of the roll having raised and recessed portions, relative to the total area of the nonwoven web.

[0056] For the purpose of improving transportability and controlling the thickness of the nonwoven fabric, the nonwoven web before thermal bonding can be temporarily bonded under a linear pressure of 50 to 700 N/cm with calender rolls at 70 to 120°C. The calender rolls may be a combination of upper and lower metal rolls or of a metal roll with a resin or paper roll.

EXAMPLES

[0057] The present invention will be specifically illustrated with reference to Examples. However, the present invention is not limited to these Examples. Various alterations and modifications are possible without departing from the technical scope of the present invention.

Measurement Methods

[0058] (1) Melt Flow Rate (MFR) (g/10 Min)

[0059] The MFRs of the resins used were measured in accordance with ASTM D1238-70 under the conditions of a measurement temperature of 315°C, and an applied load of 5 kg.

(2) Average Single Fiber Fineness (dtex)

[0060] Ten small samples were randomly taken from the nonwoven web collected on a net. The surfaces of the samples were photographed at a magnification of 500 to 1000 times under a microscope. The widths of ten fibers of each sample, 100 fibers in total, were measured and the average value was calculated. The fibers were regarded as having a circular cross section, and therefore the average width value of the single fiber was regarded as the average diameter thereof. From the average diameter and the solid density of the resin used, the weight of the single fiber per 10,000 m in length was calculated and rounded off to the first decimal place to determine the average single fiber fineness.

(3) Spinning Rate (m/min)

[0061] The spinning rates V (m/min) were calculated based on the following formula using the average single fiber fineness F (dtex) and the discharge rate of the resin per spinneret hole D (hereinafter abbreviated to discharge rate per hole: g/min) under various settings.

\[ V = \frac{10000 D F}{P} \]

(4) Crystallinity

[0062] Fibers were taken from the nonwoven web collected on a net and were embedded in a resin (a bisphenol epoxy resin, curing time: 24 hours). The embedded fibers were sectioned with a microtome to prepare a sample of a fiber cross section with a thickness of 2.0 This sample was analyzed by laser Raman spectroscopy under the conditions described below. From the obtained Raman spectrum, the full width at half maximum of the phenyl ring-S stretching band (around 1080 cm⁻¹) was determined. The full width at half maximum of the phenyl ring-S stretching band (around 1080 cm⁻¹) in the Raman spectrum of PPS becomes smaller as crystallization proceeds with the increase in structural order and the equalization of the environment around the vibration. Based on this tendency, the determined value of the full width at half maximum was used to evaluate the crystallinity (a smaller full width at half maximum means a higher crystallinity).

[0063] Device: Near-infrared Raman spectrometer (Photon Design)

[0064] Conditions:

[0065] Measurement mode: Raman microscope

[0066] Objective lens: ×100

[0067] Beam diameter: 1 μm

[0068] Cross slit: 200 μm

[0069] Light source: YAG laser/1064 nm

[0070] Laser power: 1 W

[0071] Diffraction grating: Single 300

[0072] (Full width at half maximum: 900) gr/μm

[0073] Slit: 100 μm
[0074] Detector: InGaAs/Nippon Roper Raman spectrometer

[0075] Measurement Position:

[0076] (1) Surface of the fiber (the region from 0 to 1.0 μm in the radially inward direction of the fiber when the surface is the base point (0))

[0077] (2) Center of the cross section of the fiber (diameter/2)

(5) Mass Per Unit Area (g/m²) of Nonwoven Fabric

[0078] In accordance with JIS L 1913 (2010) 6.2 “Mass per unit area”, three test pieces each having a size of 20 cm x 25 cm were taken per meter of width of a sample, the masses (g) of the test pieces in standard conditions were measured, and the average value thereof was expressed in terms of mass per m² (g/m²).

(6) Product of Strength and Elongation Per Mass Per Unit Area of Nonwoven Fabric

[0079] In accordance with JIS L 1913 (2010) 6.3.1, three test samples long in the longitudinal direction of the fabric were taken, and tensile strength test was performed on each of the test samples under the conditions of a sample size of 5 cm x 30 cm, a clamp distance of 20 cm, and a stretching rate of 10 cm/min to determine the strength at break of the sample. The determined strength at break was taken as the longitudinal tensile strength (N/5 cm). The elongation of the sample at the maximum load was also measured at an accuracy of 1 mm to determine the elongation rate (i.e., the length elongated from the original length). The determined elongation rate was taken as the longitudinal tensile elongation (%). The average of the determined longitudinal tensile strength (N/5 cm) and the average of the determined longitudinal tensile elongation (%) were calculated and rounded off to the whole number. Then, from the longitudinal tensile strength (N/5 cm) and the longitudinal tensile elongation (%) calculated in this manner, and the mass per unit area (g/m²) determined in the above (5), the product of strength and elongation per mass per unit area was calculated by the following formula and rounded off to the whole number.

[0080] \[ \text{Product of strength and elongation per mass per unit area} = \text{longitudinal tensile strength (N/5 cm)} \times \text{longitudinal tensile elongation (%)} \times \frac{\text{mass per unit area (g/m²)}}{100} \]

(7) Thermal Shrinkage Rate (%) of Nonwoven Fabric

[0081] In accordance with JIS L 1913 (2010) 6.10.3 “Dimensional change rate under dry heat conditions”, the measurement was performed. The inside temperature of a constant temperature dryer was set at 200°C and heat treatment was performed for 10 minutes.

Example 1

Component A

[0082] A 100 mol % linear polyphenylene sulfide resin (Toray Industries, Inc., product number: E2280, MFR: 160 g/10 min) was dried in nitrogen atmosphere at 160°C for 10 hours and used as component A.

Component B

[0083] A 100 mol % linear polyphenylene sulfide resin (Toray Industries, Inc., product number: M2588, MFR: 300 g/10 min) was dried in nitrogen atmosphere at 160°C for 10 hours and used as component B.

Spinning and Nonwoven Web Forming

[0084] The component A was melted in an extruder for a core component, and the component B was melted in an extruder for a sheath component. The components A and B were metered to provide an A:B mass ratio of 80:20. The components were spun from a rectangular-shaped core-sheath spinneret with a hole diameter (Φ) of 0.55 mm at a discharge rate per hole of 1.37 g/min at a spinning temperature of 315°C to form continuous core-sheath composite fibers. The spun fibers were cooled and solidified in an atmosphere at a room temperature of 20°C, and were passed through a rectangular ejector disposed at a distance of 350 mm from the spinneret. The fibers were drawn and stretched by the air that was heated to 200°C with an air heater and ejected from the ejector at an ejector pressure of 0.17 MPa. The drawn fibers were collected on a moving net to form a nonwoven web. The obtained core-sheath composite long fibers had an average single fiber fineness of 2.9 dtex. The spinning rate was 4,797 m/min. The crystallinity was lower in the surface of the fibers than in the center of the cross section of the fibers. The occurrence of the breakage of the fibers during 1 hour spinning was zero and thus good spinnability was observed.

Temporary Bonding and Thermal Bonding

[0085] The nonwoven web was then temporarily bonded under a linear pressure of 200 N/cm and at a temporary bonding temperature of 90°C using a pair of upper and lower metal calendaring rolls installed in the production line. The nonwoven fabric was then thermally bonded under a linear pressure of 1000 N/cm and at a thermal bonding temperature of 200°C using an embossing roll pair which provided a 12% bonded area and which consisted of an upper metal roll having a polka-dot emboss pattern and a lower flat metal roll, to give a core-sheath composite long-fiber nonwoven fabric. The obtained core-sheath composite long-fiber nonwoven fabric had a mass per unit area of 260 g/m², a product of strength and elongation per mass per unit area of 54 and thermal shrinkage rates of 0.1% in the longitudinal direction and 0.0% in the transverse direction.

Example 2

Component A

[0086] The same PPS resin as in Example 1 was used as component A.

Component B

[0087] The same PPS resin as in Example 1 was used as component B.

Spinning and Nonwoven Web Forming

[0088] Core-sheath composite spinning and nonwoven web forming were performed in the same manner as in Example 1 except that the ejector pressure was 0.15 MPa. The obtained core-sheath composite long fibers had an average single fiber fineness of 3.2 dtex. The spinning rate was 4,317 m/min. The crystallinity was lower in the surface of the fibers than in the center of the cross section of the fibers. The occurrence of the breakage of the fibers during 1 hour spinning was zero and thus good spinnability was observed.
Temporary Bonding and Thermal Bonding

The nonwoven web was temporarily and thermally bonded to give a core-sheath composite long-fiber nonwoven fabric in the same manner as in Example 1. The obtained core-sheath composite long-fiber nonwoven fabric had a mass per unit area of 260 g/m², a product of strength and elongation per mass per unit area of 51, and thermal shrinkage rates of 0.1% in the longitudinal direction and 0.1% in the transverse direction.

Example 3

Component A

The same PPS resin as in Example 1 was used as component A.

Component B

The same PPS resin as in Example 1 was used as component B.

Spinning and Nonwoven Web Forming

Core-sheath composite spinning and nonwoven web forming were performed in the same as in Example 1. The obtained core-sheath composite long fibers had an average single fiber fineness of 2.9 dtex. The spinning rate was 4,797 m/min. The crystallinity was lower in the surface of the fibers than in the center of the cross section of the fibers. The occurrence of the breakage of the fibers during 1 hour spinning was zero and thus good spinnability was observed.

Comparative Example 1

Component A

The same PPS resin as in Example 1 was used as component A.

Component B

Component B was not used.

Temporary Bonding and Thermal Bonding

The nonwoven web was temporarily and thermally bonded to give a core-sheath composite long-fiber nonwoven fabric in the same manner as in Example 1 except that the thermal bonding temperature was 140°C. The obtained core-sheath composite long-fiber nonwoven fabric had a mass per unit area of 260 g/m², a product of strength and elongation per mass per unit area of 62 and thermal shrinkage rates of 0.1% in the longitudinal direction and 0.0% in the transverse direction.

Example 4

Component A

The same PPS resin as in Example 1 was used as component A.

Component B

The same PPS resin as in Example 1 was used as component B.

Spinning and Nonwoven Web Forming

Core-sheath composite spinning and nonwoven web forming were performed in the same manner as in Example 1 except that the thermal bonding temperature was 240°C. The obtained core-sheath composite long-fiber nonwoven fabric had a mass per unit area of 260 g/m², a product of strength and elongation per mass per unit area of 50 and thermal shrinkage rates of 0.1% in the longitudinal direction and 0.1% in the transverse direction.

Temporary Bonding and Thermal Bonding

The nonwoven web was temporarily and thermally bonded to give a core-sheath composite long-fiber nonwoven fabric in the same manner as in Example 1 except that the thermal bonding temperature was 240°C. The obtained core-sheath composite long-fiber nonwoven fabric had an average single fiber fineness of 2.9 dtex. The spinning rate was 4,797 m/min. The crystallinity was lower in the surface of the fibers than in the center of the cross section of the fibers. The occurrence of the breakage of the fibers during 1 hour spinning was zero and thus good spinnability was observed.

Temporary Bonding and Thermal Bonding

The nonwoven web was temporarily and thermally bonded to give a core-sheath composite long-fiber nonwoven fabric in the same manner as in Example 1 except that the thermal bonding temperature was 315°C. The spinning and nonwoven web forming were performed in the same manner as in Example 2. The obtained single-component long fibers had an average single fiber fineness of 2.4 dtex. The spinning rate was 4,920 m/min. The crystallinity was higher in the surface of the fibers than in the center of the cross section of the fibers. The occurrence of the breakage of the fibers during hour spinning was zero and thus good spinnability was observed.

Temporary Bonding and Thermal Bonding

The nonwoven web was temporarily and thermally bonded to give a single-component long-fiber nonwoven fabric in the same manner as in Example 1 except that the thermal bonding temperature of the embossing roll pair was 260°C. The obtained single-component long-fiber nonwoven fabric had an average mass per unit area of 260 g/m², a product of strength and elongation per mass per unit area of 4 and thermal shrinkage rates of 0.0% in the longitudinal direction and 0.1% in the transverse direction.

| TABLE 1 |
|--------|--------|--------|--------|--------|--------|
| Resin Component | Melting point | MFR g/10 min |
| A | C | 1 | 2 | 3 | 4 | 1 |
| — | — | 281 | 281 | 281 | 281 | 281 |
| Example 1 | Example 2 | Example 3 | Example 4 | Example 1 |
### Table 1-continued

<table>
<thead>
<tr>
<th>Component</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
<th>Comparative Example 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>281</td>
<td>281</td>
<td>281</td>
<td>281</td>
<td>281</td>
</tr>
<tr>
<td>MFR (g/10 min)</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Mass ratio</td>
<td>80:20</td>
<td>80:20</td>
<td>80:20</td>
<td>80:20</td>
<td>100:0</td>
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<tr>
<td>Spinning temperature</td>
<td>315</td>
<td>315</td>
<td>315</td>
<td>315</td>
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</tr>
<tr>
<td>Spinning hole diameter</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td>0.50</td>
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<tr>
<td>Discharge rate per spinning hole (g/min)</td>
<td>1.37</td>
<td>1.37</td>
<td>1.37</td>
<td>1.37</td>
<td>1.37</td>
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<tr>
<td>Temperature of compressed air (°C)</td>
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<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Ejector pressure (MPa)</td>
<td>0.17</td>
<td>0.15</td>
<td>0.17</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>Average single fiber fineness (dtx)</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Spinning rate (m/min)</td>
<td>4920</td>
<td>4797</td>
<td>4797</td>
<td>4797</td>
<td>4920</td>
</tr>
<tr>
<td>Full width of fiber at half maximum of cross section of fiber</td>
<td>12.8</td>
<td>13.3</td>
<td>12.8</td>
<td>12.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Temporary bonding temperature (°C)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Thermal bonding temperature (°C)</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Linear pressure (N/cm)</td>
<td>200</td>
<td>200</td>
<td>140</td>
<td>200</td>
<td>260</td>
</tr>
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<td>Nonwoven fabric mass per unit area (g/m²)</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Product of strength and elongation per mass per unit area (g/m²)</td>
<td>54</td>
<td>51</td>
<td>62</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>Thermal shrinkage</td>
<td>% 0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Transverse rate (%)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

As shown in Table 1, Examples 1 to 4, in which the PPS of the sheath component had a lower viscosity than the PPS of the core component, had a lowered crystallinity on the surface of the fibers. The core-sheath composite long-fiber nonwoven fabrics made therefrom had greatly improved values of the product of strength and elongation per mass per unit area and more excellent mechanical strength, as compared with the single-component long-fiber nonwoven fabric of Comparative Example 1.

The nonwoven fabric made from the thermally bonding composite fiber of the present invention has both thermal dimensional stability and excellent mechanical strength, and is therefore suitable for various industrial filters, electric insulating materials, battery separators, membrane materials for water treatment, heat insulating materials, hazmat suits, and the like.

1. A polyphenylene sulfide composite fiber consisting primarily of component A and component B, the component A being a resin that comprises polyphenylene sulfide as its main constituent, the component B being a resin that comprises polyphenylene sulfide as its main constituent, having a higher melt flow rate than the component A, and forming at least part of the surface of the fiber.

2. The polyphenylene sulfide composite fiber according to claim 1, wherein at least part of the surface of the fiber has a lower crystallinity than the center of the cross section of the fiber when the crystallinity of the fiber surface is measured in the region from the fiber surface to 1 µm in the radially inward direction of the fiber.

3. The polyphenylene sulfide composite fiber according to claim 1 or 2, wherein the melt flow rate of the component A (MFR(A)) and the melt flow rate of the component B (MFR(B)) satisfy the following formula:

\[10 (g/10 min) \times MFR(A) - MFR(A) \times 1000 (g/10 min)\]

4. The polyphenylene sulfide composite fiber according to claim 1 or 2, which is a core-sheath composite fiber comprising the component A as a core component and the component B as a sheath component.

5. A nonwoven fabric made from the polyphenylene sulfide composite fiber according to claim 1 or 2.

6. The nonwoven fabric according to claim 5, which is a spunbonded nonwoven fabric.

7. The nonwoven fabric according to claim 6, which is produced by integrating the polyphenylene sulfide composite fiber by thermal bonding.

* * * *