(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 716 800 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.04.2014 Bulletin 2014/15

(21) Application number: **12792614.5**

(22) Date of filing: **01.06.2012**

(51) Int Cl.:
D01F 6/76 $^{(2006.01)}$ ***D04H 3/009*** $^{(2012.01)}$
D04H 3/08 $^{(2006.01)}$ ***D04H 3/14*** $^{(2012.01)}$

(86) International application number:
PCT/JP2012/064256

(87) International publication number:
WO 2012/165608 (06.12.2012 Gazette 2012/49)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **02.06.2011 JP 2011123994**

(71) Applicant: **Toray Industries, Inc.**
Tokyo 103-8666 (JP)

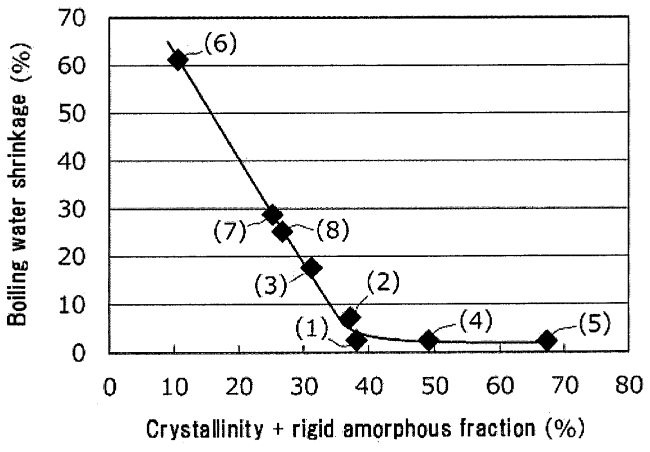
(72) Inventors:
- **NAKANO, Yohei**
  Otsu-shi
  Shiga 520-8558 (JP)
- **YAKAKE, Yoshikazu**
  Otsu-shi
  Shiga 520-8558 (JP)
- **ITO, Masashi**
  Otsu-shi
  Shiga 520-8558 (JP)

(74) Representative: **Kador & Partner**
Corneliusstrasse 15
80469 München (DE)

(54) POLYPHENYLENE SULFIDE FIBERS AND NONWOVEN FABRIC

(57) Provided are a polyphenylene sulfide fiber comprising a PPS resin as a main component and having both excellent heat resistance and excellent thermal bonding properties, and a nonwoven fabric comprising the fiber. The polyphenylene sulfide fiber comprises polyphenylene sulfide as a main component and having the sum of the crystallinity and the rigid amorphous fraction of 30% to 90%. The crystallinity is preferably not less than 5% and less than 25%. The polyphenylene sulfide fiber is used to form a nonwoven fabric. The nonwoven fabric is preferably produced by consolidation by thermal bonding or mechanical entanglement.

Fig. 2



Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a fiber comprising a resin comprising polyphenylene sulfide (hereinafter sometimes abbreviated to "PPS") as a main component, and a nonwoven fabric comprising the fiber.

BACKGROUND ART

[0002] PPS resins are excellent in heat resistance, flame retardancy and chemical resistance and are therefore suitably used as engineering plastics, films, fibers, nonwoven fabrics, or the like. Especially nonwoven fabrics utilizing these excellent properties are expected to be used in industrial applications such as heat-resistant filters, electrical insulation materials, and battery separators.

[0003] However, in cases where a PPS resin is spun into fibers to form a nonwoven fabric, problems may arise concerning poor thermal dimensional stability, which may lead to significant thermal shrinkage of the fibers or the nonwoven fabric.

[0004] In order to improve the dimensional stability of PPS nonwoven fabrics, there has been proposed, for example, a filament nonwoven fabric produced by spun bonding in which a PPS resin is spun and drawn into filaments, the filaments are temporarily bonded at a temperature not more than the first crystallization temperature of the fabric to be produced, the obtained fabric is subjected to heat treatment under strain at a temperature not less than the first crystallization temperature to promote the crystallization of the filaments, and the fabric is subjected to permanent bonding (see, for example, Patent Literature 1). There has also been proposed a heat-resistant nonwoven fabric produced by spinning and drawing a PPS resin at a high spinning speed of 6,000 m/min or more to promote the crystallization of the fibers, and thereby to suppress thermal shrinkage (see, for example, Patent Literature 2). These proposals, however, suffer from poor thermal bonding properties.

[0005] Thus there has been no proposal for a PPS fiber or PPS nonwoven fabric having both heat resistance and thermal bonding properties.

CITATION LIST

PATENT LITERATURE

[0006]

Patent Literature 1: JP-2008-223209 A
Patent Literature 2: WO 2008/035775

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0007] In consideration of the above problems in the conventional art, an object of the present invention is to provide a fiber comprising a PPS resin as a main component and having both excellent heat resistance and excellent thermal bonding properties, and a nonwoven fabric comprising the fiber.

SOLUTION TO PROBLEM

[0008] The reason conventional techniques as described above cannot achieve heat resistance and thermal bonding properties at the same time is probably that promotion of crystallization leads to increase in the thermal dimensional stability on the one hand and, on the other hand, to decrease in the amorphous phase, which can melt and contribute to thermal bonding. The inventors conducted intensive research to simultaneously achieve the above properties that seem incompatible and, as a result, found the following means.

[0009] That is, a first aspect of the present invention relates to a polyphenylene sulfide fiber comprising polyphenylene sulfide as a main component and having the sum of the crystallinity and the rigid amorphous fraction of 30% to 90%.

[0010] A second aspect of the present invention relates to a nonwoven fabric comprising the polyphenylene sulfide fiber according to the first aspect of the present invention.

[0011] The polyphenylene sulfide fiber (hereinafter also referred to as PPS fiber) of the first aspect of the present invention having the sum of the crystallinity and the rigid amorphous fraction of 30% or more, preferably 35% or more, is excellent in thermal dimensional stability. The polyphenylene sulfide fiber having the sum of the crystallinity and the rigid amorphous fraction of 90% or less, more preferably 70% or less, still more preferably 50% or less, is preferred in terms of thermal bonding properties.

[0012] The crystallinity is not limited to a specific range. However, the crystallinity is preferably 5% or more, more preferably 10% or more, and still more preferably 15% or more. When a nonwoven web of the fiber having such crystallinity is thermally bonded, the resulting sheet is prevented from breakage due to being wound up around a roll. The crystallinity is preferably less than 25%, more preferably 23% or less, and still more preferably 20% or less so that a large amount of the amorphous phase (including the rigid amorphous fraction) is present in the fiber and contributes to excellent thermal bonding properties for thermal bonding of the nonwoven web.

[0013] As regards the above-mentioned nonwoven fabric, a production method therefor and the structure thereof are not particularly limited. For example, the nonwoven fabric can be produced by spun bonding in which the PPS fibers are consolidated by thermal bonding or mechanical entanglement.

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] The PPS fiber of the present invention has excellent thermal bonding properties while maintaining the properties of a PPS resin, namely, heat resistance, chemical resistance, and flame retardancy. Consequently, the nonwoven fabric of the present invention also has excellent mechanical strength while maintaining the properties of a PPS resin, namely, heat resistance, chemical resistance, and flame retardancy and is therefore usable for various industrial applications.

BRIEF DESCRIPTION OF DRAWINGS

[0015]

Fig. 1 is a graph showing the relation of the boiling water shrinkage to the crystallinity in PPS fibers.

Fig. 2 is a graph showing the relation of the boiling water shrinkage to the sum of the crystallinity and the rigid amorphous fraction in PPS fibers.

DESCRIPTION OF EMBODIMENTS

[0016] The resin used in the present invention comprises PPS as a main component. Hereinafter, the resin that is used in the present invention and comprises PPS is also referred to as the "PPS resin".

[0017] PPS is a polymer having, as the repeating unit, a phenylene sulfide unit such as a p-phenylene sulfide unit and a m-phenylene sulfide unit. Preferred is a substantially linear polymer containing 90 mol% or more of a p-phenylene sulfide unit because of its heat resistance and spinnability. In cases where PPS is used as a main component to obtain a polymer with a low melting point, preparation of a polymer by copolymerization of a p-phenylene sulfide unit with a m-phenylene sulfide unit is preferred in that the flame retardancy and chemical resistance of PPS are not impaired. The copolymerized PPS can be suitably used as a component for a composite fiber.

[0018] Preferably, PPS is substantially not copolymerized with trichlorobenzene. This is because trichlorobenzene has three or more halogen substituents per benzene ring and thus the copolymerization of PPS with trichlorobenzene results in a branched structure, leading to poor spinnability of the resulting PPS resin and frequent breakage of the resulting fibers during spinning and drawing. The copolymerized trichlorobenzene content, as the degree of being substantially free from copolymerized trichlorobenzene, is preferably 0.05 mol% or less, and more preferably 0.01 mol% or less.

[0019] The PPS content of the PPS resin is preferably 85% by mass or more, more preferably 90% by mass or more, and still more preferably 95% by mass or more in view of heat resistance, chemical resistance, and the like. To the PPS resin may be added a nucleator, a matting agent, a pigment, an antifungal agent, an antibacterial agent, a flame retardant, a hydrophilic agent, and/or the like to the extent that these do not impair the effects of the present invention.

[0020] The PPS resin used in the present invention preferably has a melt flow rate (hereinafter sometimes abbreviated to MFR) measured in accordance with ASTM D1238-70 (measurement temperature: 315.5°C, measurement load: 5 kg) of 100 to 300 g/10 min. The PPS resin having an MFR of 100 g/10 min or more, more preferably 140 g/10 min or more, has moderate fluidity, which contributes to the suppression of increase in the back pressure of the spinneret during melt spinning and to the prevention of breakage of the resulting fibers during pulling and drawing. The PPS resin having an MFR of 300 g/10 min or less, more preferably 225 g/10 min or less, has a moderately high polymerization degree or molecular weight, which contributes to increase in strength and heat resistance sufficient for practical use.

[0021] It is important for the PPS fiber of the present invention to have the sum of the crystallinity and the rigid amorphous fraction of 30% to 90%.

[0022] The crystallinity herein refers to those determined by measuring with a differential scanning calorimetry (DSC) as described later in Examples.

[0023] The rigid amorphous fraction herein refers to the remainder left after subtraction of the crystallinity [%] and the mobile amorphous fraction [%] from the total of the crystal and amorphous fractions (100%) that constitutes the fiber, as shown in the following formula:

$$\text{Rigid amorphous fraction [\%]} = 100\ [\%] - \text{crystallinity [\%]} - \text{mobile amorphous fraction [\%]}.$$

[0024] The mobile amorphous fraction herein refers to those determined by measuring with a temperature modulated DSC as described later in Examples.

[0025] The inventors found that not only the crystal fraction but also the rigid amorphous fraction significantly affects the thermal dimensional stability.

[0026] That is, as shown in the relation of the boiling water shrinkage to the crystallinity in Fig. 1, even though the crystallinity values are substantially the same among the samples having a crystallinity of less than 20%, the boiling water shrinkage greatly varies; however, as shown in the relation of the boiling water shrinkage to the sum of the crystallinity and the rigid amorphous fraction in Fig. 2, when the rigid amorphous fraction is used as an evaluation factor in addition to the crystallinity, a strong correlation is observed, which reveals that the rigid amorphous fraction significantly affects the thermal dimensional stability. Although the mechanism is unclear, the rigid amorphous fraction is an amorphous yet is considered to play a similar role to that of the crystal fraction for the thermal dimensional stability.

[0027] In Figs. 1 and 2, the data is based on Examples and Comparative Examples described later, and the numbers within the brackets in the graphs correspond to the numbers in Table 1 described later.

[0028] As shown in Fig. 2, the boiling water shrinkage is less than 20% when the sum of the crystallinity and the rigid amorphous fraction is 30% or more, and the boiling water shrinkage is less than 10% when the sum of the crystallinity and the rigid amorphous fraction is 35% or more.

[0029] In view of suppression of shrinkage in width, wrinkles, and surface irregularity caused by thermal shrinkage, the boiling water shrinkage is preferably 20% or less, more preferably 15% or less, and still more preferably 10% or less. Consequently, a fiber having the sum of the crystallinity and the rigid amorphous fraction of 30% or more, preferably 35% or more, has excellent thermal dimensional stability.

[0030] In view of thermal bonding properties, in addition to the rigid amorphous fraction, preferably the mobile amorphous fraction is also contained in an amount of 10% or more, more preferably 30% or more, still more preferably 50% or more. Although the mechanism is unclear, it is considered that, in thermal bonding, fibers comprising a certain amount of the mobile amorphous fraction more easily undergo plastic deformation in accordance with the magnitude of the pressure applied to the fibers for bonding. That is, the sum of the crystallinity and the rigid amorphous fraction in the PPS fiber is preferably 90% or less, more preferably 70% or less, and still more preferably 50% or less.

[0031] The crystallinity of the PPS fiber of the present invention is preferably not less than 5% and less than 25%.

[0032] As described in the above Patent Literature 2, it has been considered that the crystallinity needs to be 25% or more to stably impart thermal dimensional stability to a PPS fiber. However, according to the present invention, even when the crystallinity is less than 25%, thermal shrinkage of a PPS fiber can be reduced by increasing the amount of the rigid amorphous fraction. Conventionally, low crystallinity of a PPS fiber means the presence of a large amount of the amorphous phase, which results in poor thermal dimensional stability; whereas high crystallinity of a PPS fiber means the presence of a small amount of the amorphous phase, which results in poor thermal bonding properties. According to the present invention, the amorphous phase, especially the rigid amorphous fraction, is increased to impart thermal dimensional stability, thereby achieving both excellent thermal dimensional stability and excellent thermal bonding properties.

[0033] The crystallinity of the PPS fiber of the present invention is 5% or more, more preferably 10% or more, and still more preferably 15% or more. When a nonwoven web of the fiber having such crystallinity is thermally bonded, the resulting sheet is prevented from breakage due to being wound up around a roll. The crystallinity is less than 25%, more preferably 23% or less, and still more preferably 20% or less so that a large amount of the amorphous phase (including the rigid amorphous fraction) is present in the fiber and contributes to excellent thermal bonding properties for thermal bonding of the nonwoven web.

[0034] The cross section of the PPS fiber of the present invention may be any shape such as a circular shape, a hollow round shape, an oval shape, a flat shape, a polygonal shape, and a multilobal shape (such as an X shape and a Y shape).

[0035] The PPS fiber of the present invention may be in a composite form. Examples of the composite form include a core-sheath type, an eccentric core-sheath type, an Umishima type, a parallel type, a radial type, and a multilobal type. Among these, preferred is a core-sheath type, which is suitable for achieving excellent spinnability.

[0036] The average single fiber fineness of the PPS fiber of the present invention is preferably 0.5 to 10 dtex.

[0037] When spinning is performed so as to form fibers having an average single fiber fineness of 0.5 dtex or more, more preferably 1 dtex or more, still more preferably 2 dtex or more, spinnability of the fibers is assured and frequent breakage of the fibers during spinning can be prevented.

[0038] When spinning is performed so as to form fibers having an average single fiber fineness of 10 dtex or less, more preferably 5 dtex or less, still more preferably 4 dtex or less, the discharge rate of a molten resin per hole of a spinneret can be suitably reduced to allow the resulting fibers to sufficiently cool down, thereby preventing reduction in spinnability due to fusion bonding between the fibers. Moreover, when such fibers are formed into a nonwoven fabric, the variation in the mass per unit area of the nonwoven fabric can be reduced, thereby providing excellent quality for the surfaces of the nonwoven fabric. Also in view of the dust collecting performance of the nonwoven fabric used as a filter or the like, the average single fiber fineness is preferably 10 dtex or less, more preferably 5 dtex or less, and still more preferably 4 dtex or less.

[0039] The PPS fiber of the present invention can be used as a fiber for forming any type of fabric such as woven fabrics and nonwoven fabrics but, because of its excellent thermal bonding properties, the PPS fiber of the present invention can be more suitably used as a component fiber of a nonwoven fabric whose structure is fixed by thermal press-bonding.

[0040] The PPS nonwoven fabric of the present invention may be a filament nonwoven fabric or a staple nonwoven fabric, but a filament nonwoven fabric produced by spun bonding is preferred for its excellent productivity.

[0041] The mass per unit area of the nonwoven fabric of the present invention is preferably 10 to 1000 g/m^2. The nonwoven fabric having a mass per unit area of 10 g/m^2 or more, more preferably 100 g/m^2 or more, still more preferably 200 g/m^2 or more, exhibits a sufficient mechanical strength for practical use. In cases where the nonwoven fabric is used as a filter or the like, the mass per unit area is 1000 g/m^2 or less, more preferably 700 g/m^2 or less, and still more preferably 500 g/m^2 or less. The nonwoven fabric having such a mass per unit area has moderate air permeability and thus prevents pressure loss from increasing.

[0042] The thermal shrinkage rate at 200°C of the PPS nonwoven fabric of the present invention is preferably 5% or less both in the longitudinal and transverse directions. Because of its properties, PPS nonwoven fabrics are often used under high temperature. When the thermal shrinkage rate at 200°C of the PPS nonwoven fabric of the present invention is 5% or less, more preferably 3% or less, reduction in its performance due to dimensional change can be prevented, and such a PPS nonwoven fabric is suitable for practical use.

[0043] The PPS nonwoven fabric of the present invention preferably has a longitudinal tensile strength retention rate measured by a heat-exposure resistance test in the air, at 210°C for 1500 hours of 80% or more. The PPS nonwoven fabric having a longitudinal tensile strength retention rate of 80% or more, more preferably 85% or more, still more preferably 90% or more, can be used as a heat-resistant filter or the like that is used under high temperature for a long period of time. The upper limit value of the longitudinal tensile strength retention rate is not particularly limited but is preferably 150% or less.

[0044] Next, a production method for a PPS nonwoven fabric by spun bonding, which is a preferred embodiment for the PPS fiber and PPS nonwoven fabric of the present invention, will be described below.

[0045] Spun bonding is a production method that requires the steps of: melting a resin, spinning the molten resin from a spinneret, solidifying the resulting filamentary streams by cooling, pulling and drawing the filamentary streams by means of an ejector, collecting the filaments on a moving net to form a nonwoven web, and consolidating the nonwoven web by thermal bonding or mechanical entanglement.

[0046] 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 because the amount of compressed air to be used is relatively small and the filaments are hardly fusion-bonded or scratch each other.

[0047] The spinning temperature for melting and spinning PPS is preferably 290 to 380°C, more preferably 295 to 360°C, and still more preferably 300 to 340°C. The spinning temperature within the above range allows PPS to be brought into a stable molten state and to exhibit excellent spinning stability.

[0048] Examples of the method for cooling the spun filamentary streams include, for example, a method in which cold air is forced to blow over the filamentary streams, a method in which the filamentary streams are allowed to cool down at atmospheric temperature around the filamentary streams, a method in which the distance between the spinneret and the ejector is adjusted, and a combination thereof. The cooling conditions can be appropriately adjusted and adopted in consideration of the discharge rate per hole of the spinneret, the spinning temperature, the atmospheric temperature, and the like.

[0049] Next, the filamentary streams that have solidified by cooling are pulled and drawn by compressed air blown from the ejector. The method for pulling and drawing the filamentary streams by means of the ejector and the conditions therefor are not particularly limited, but a method in which the filamentary streams are pulled and drawn by compressed air heated and blown from the ejector, the compressed air being heated to 100°C or more, preferably 140°C or more, more preferably 180°C or more, is preferred in that the crystallization of the PPS fiber is suppressed and at the same time the rigid amorphous fraction is increased. Since heated compressed air is used, the filamentary streams that are being pulled and drawn are simultaneously heat treated. However, the heat treatment duration is extremely short and therefore the rigid amorphous fraction, which is an intermediate phase between the crystal phase and the amorphous phase, can be specifically increased. The upper limit of the temperature of the heated compressed air is not more than the melting point of PPS.

[0050] Another method for heat treating the filamentary streams during pulling and drawing include a method in which a heater is disposed before or after the ejector. However, this method is not preferred because the thermal conductivity is inferior to that in the above method in which a hot air of high temperature is directly blown over the fibers, and consequently the heat does not contribute to increase in the rigid amorphous fraction.

[0051] The spinning speed is preferably not less than 3,000 m/min and less than 6,000 m/min. Spinning at a spinning speed of 3,000 m/min or more, more preferably 3,500 m/min or more, still more preferably 4,000 m/min or more, can produce a PPS fiber having high crystallinity. Consequently, when a resulting nonwoven web is thermally bonded, the resulting sheet is prevented from breakage due to being wound up around a roll. Spinning at a spinning speed less than 6,000 m/min is preferred because excessive increase in the crystallinity can be prevented and excellent spinning stability can be achieved.

[0052] Next, the PPS fibers obtained by drawing are collected on a moving net to form a nonwoven web, and the obtained nonwoven web is consolidated by thermal bonding or mechanical entanglement to form a nonwoven fabric.

[0053] Preferred method for consolidation into a nonwoven fabric are a thermal bonding method in which thermal press-bonding is performed using various types of rolls such as a roll pair for thermal embossing that is composed of upper and lower rolls each having embossment on their surfaces, a roll pair for thermal embossing that is composed of a roll having a flat (smooth) surface and a roll having embossment on its surface, or a roll pair for thermal calendering that is composed of upper and lower flat (smooth) rolls; and a mechanical entanglement method using needle punching or water jet punching.

[0054] In cases where thermal press-bonding is performed with a thermal embossing roll pair, the embossment pattern on the embossing roll(s) may be circle, oval, square, rectangle, parallelogram, diamond, regular hexagon, or regular octagon, or the like.

[0055] The surface temperature of the thermal embossing roll pair is preferably 5 to 30°C lower than the melting point of PPS. By means of the thermal embossing roll pair having a surface temperature not lower than the temperature that is 30°C lower than the melting point of PPS, more preferably a surface temperature not lower than the temperature that is 25°C lower than the melting point of PPS, still more preferably a surface temperature not lower than the temperature that is 20°C lower than the melting point of PPS, the nonwoven web is thermally bonded to a sufficient extent and thereby flaking off and fluffing of the resulting nonwoven fabric can be prevented. By means of the thermal embossing roll pair having a surface temperature not higher than the temperature that is 5°C lower than the melting point of PPS, perforation in the press-bonded parts due to fusion of the fibers can be prevented.

[0056] The linear pressure applied by the thermal embossing roll pair during thermal bonding is preferably 200 to 1500 N/cm. By means of the rolls with a linear pressure of 200 N/cm or more, more preferably 300 N/cm or more, the nonwoven web is thermally bonded to a sufficient extent and thereby flaking off and fluffing of the resulting sheet can be prevented. By means of the rolls with a linear pressure of 1500 N/cm or less, more preferably 1000 N/cm or less, the raised portions of the embossment are prevented from biting into the nonwoven fabric and thereby trouble removing the nonwoven fabric from the rolls or the breakage of the nonwoven fabric can be prevented.

[0057] The bonding area provided by means of the thermal embossing roll pair is preferably 8 to 40%. Thermal bonding with the roll pair so as to provide a bonding area of 8% or more, more preferably 10% or more, still more preferably 12% or more, can produce a nonwoven fabric having a sufficient strength for practical use. Thermal bonding with the roll pair so as to provide a bonding area of 40% or less, more preferably 30% or less, still more preferably 20% or less, can prevent the resulting nonwoven fabric from being formed into a film-like shape that hardly has the advantages of a nonwoven fabric, such as air permeability. When thermal bonding is performed with a pair of upper and lower rolls each having raised and recessed portions, the bonding area herein refers to the ratio of the area where the nonwoven web is 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 fabric. When thermal bonding is performed with a pair of a roll having raised and recessed portions and a flat roll, the bonding area herein refers to the ratio of the area where the nonwoven web is in contact with the raised portions of the roll having raised and recessed portions, relative to the total area of the nonwoven fabric.

[0058] When the nonwoven fabric is mechanically entangled by needle punching, the shape of the needles and the number of needles per unit area can be appropriately selected and adjusted to perform the entanglement. In particular, the number of needles per unit area is preferably at least 100 per cm^2 or more in view of the strength and the retention of the shape of the needles. Preferably, a silicone-based oil agent is sprayed on the nonwoven web before needle punching to prevent cutting of the fibers with the needles and to enhance the entanglement of the fibers. '

[0059] When the mechanical entanglement is performed by water jet punching, columnar jets of water is preferably used. Usually, for creating columnar jets of water, a method in which water is forced out of nozzles 0.05 to 3.0 mm in diameter at a pressure of 1 to 60 MPa is suitably used. For achieving efficient entanglement and consolidation of the nonwoven web, the nonwoven web is preferably treated, at least once, at a pressure of 10 MPa or more, more preferably 15 MPa or more.

[0060] For the purpose of improving transportability and controlling the thickness of the nonwoven fabric, the nonwoven web before thermal bonding or mechanical entanglement can be temporarily bonded with calender rolls at 70 to 170°C and at a linear pressure of 50 to 700 N/cm. The calender rolls may be a combination of upper and lower metallic rolls or of a metallic roll with a resin or paper roll.

[0061] Furthermore, for the purpose of improving the thermal stability, the nonwoven web before thermal bonding or before or after mechanical entanglement or the nonwoven fabric can be heat treated under strain using a pin tenter, a clip tenter, or the like, or heat treated without strain (under a strain-free condition) using a hot air dryer or the like. The temperature for the heat treatment is preferably in the range of from the crystallization temperature to the melting point of the PPS fiber that forms the nonwoven web or nonwoven fabric.

EXAMPLES

Measurement methods

(1) Melt flow rate (MFR) (g/10 min)

[0062] The MFR of PPS was measured in accordance with ASTM D1238-70 under the conditions of a measurement temperature of 315.5°C and a measurement load of 5 kg.

(2) Average single fiber fineness (dtex)

[0063] Ten pieces of small samples were randomly taken from a 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 out of each sample, 100 fibers in total, were measured and the average values were calculated. The fibers are regarded as fibers having a circular cross section, and therefore the average width values of the single fibers were regarded as the average diameter thereof. From the average width values, the weights of the single fibers for each 10,000 m in length were calculated based on the solid density of the resin used and rounded off to the first decimal place to determine average single fiber finenesses.

(3) Spinning speed (m/min)

[0064] The spinning speed was calculated based on the following formula using the average single fiber fineness (dtex) of a fiber and the discharge rate of the resin per hole of a spinneret having various settings (hereinafter abbreviated to discharge rate per hole) (g/min).

$$\text{Spinning speed} = (10000 \times \text{discharge rate per hole})/\text{average single fiber fineness}$$

(4) Crystallinity (%)

[0065] Three samples were randomly taken from fibers after drawing. The samples were subjected to measurement with a differential scanning calorimetry (Q1000, made by TA Instruments, Inc.) under the following conditions. The crystallinity of each sample was then determined by the following formula and the average value thereof was calculated. In the formula, the term "exothermic heat of cold crystallization" refers to the exothermic peak area resulting from cold crystallization, and the term "endothermic heat of fusion" refers to the endothermic peak area resulting from fusion. The baseline for the calculation of the heat (peak area) was a straight line connecting the heat flow curve in the liquid phase after the glass transition of the amorphous phase and the heat flow curve in the liquid phase after crystal fusion. The baseline intersects the DSC curve and separates the exothermic side from the endothermic side. The heat of fusion of a perfect crystal was 146.2 J/g.

- Measurement atmosphere: nitrogen flow (50 ml/min)
- Temperature range: 0 to 350°C
- Heating rate: 10°C/min
- Amount of sample: 5 mg

$$\text{Crystallinity} = \{[(\text{endothermic heat of fusion [J/g]}) - (\text{exothermic heat of cold crystallization [J/g]})]/146.2\ [\text{J/g}]\} \times 100$$

(5) Mobile amorphous fraction (%)

[0066] Three samples were randomly taken from fibers after drawing. The samples were subjected to measurement with a temperature modulated DSC (Q1000, made by TA Instruments, Inc.) under the following conditions. The mobile amorphous fraction in each sample was determined by the following formula and the average value thereof was calculated. The specific heat of a perfect amorphous solid was 0.2699 J/g·°C.

- Measurement atmosphere: nitrogen flow (50 ml/min)
- Temperature range: 60 to 200°C
- Heating rate: 2°C/min
- Amount of the sample: 5 mg

$$\text{Mobile amorphous fraction [\%]} = (\text{change in specific heat between before and after glass transition temperature [J/g·°C]})/0.2699\ [\text{J/g·°C}] \times 100$$

(6) Rigid amorphous fraction (%)

[0067] From the crystallinity determined in the above (5) and the mobile amorphous fraction determined in the above (6), the rigid amorphous fraction was calculated by the following formula:

$$\text{Rigid amorphous fraction [\%]} = 100\ [\%] - \text{crystallinity [\%]} - \text{mobile amorphous fraction [\%]}.$$

(7) Boiling water shrinkage (%)

[0068] The fibers after drawing were randomly taken out, and five fibers were aligned parallel to each other to give one sample (length: about 10 cm). A load as described below was applied to the sample and the length (L0) was measured. Then, the sample was immersed in boiling water in a strain-free state for 20 minutes, taken out from the boiling water, and allowed to dry. The same load as above was applied to the sample again and the length (L1) was measured. From the lengths L0 and L1, the boiling water shrinkage was calculated and the average value of four samples was determined. The formulas for calculating the load and the boiling water shrinkage are shown below. The load was rounded off to the second decimal place.

$$\text{Load (g)} = 0.9 \times \text{discharge rate per hole (g/min)}$$

$$\text{Boiling water shrinkage (\%)} = \{(L0 - L1)/L0\} \times 100$$

(8) Mass per unit area (g/m^2) of nonwoven fabric

[0069] In accordance with 6.2 "Mass per unit area (ISO method)" in JIS L 1913: 2010 "Test methods for nonwovens", three test pieces having a size of 20 cm x 25 cm were taken per meter in width from each 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 m^2 (g/m^2).

(9) Tensile strength of nonwoven fabric

[0070] In accordance with 6.3.1 "In standard conditions" of 6.3 "Tensile strength and elongation rate (ISO method)" in JIS L 1913: 2010 "Test methods for nonwovens", tensile test was performed at three points in the longitudinal direction of a sample under the conditions of a sample size of 5 cm x 30 cm, a holding interval of 20 cm, and a tensile rate of 10 cm/min. The average value of the strengths at which the samples broke was determined as a longitudinal tensile strength (N/5 cm) and rounded off to the whole number.

(10) Thermal shrinkage rate (%) of nonwoven fabric

[0071] In accordance with 6.10.3 "Dimensional change rate under dry heat conditions" of 6.10 "Dimensional change rate (JIS method)" in JIS L 1913: 2010 "Test methods for nonwovens", the measurement was performed. The temperature inside a constant temperature dryer was 200°C and heat treatment was performed for 10 minutes.

(11) Heat-exposure resistance test and longitudinal tensile strength retention rate

[0072] Several necessary quantity of longitudinal samples having a size of 30 cm in length and 5 cm in width were placed in a hot air oven (TABAI SAFETY OVEN SHPS-222, made by ESPEC Corp.) and exposed to hot air at 210°C for 1500 hours at an air circulation rate of 300 L/min. The tensile strengths of the samples before and after the heat-exposure resistance test were measured by the method described in the above (9), and the longitudinal tensile strength retention rates were calculated by the following formula:

Longitudinal tensile strength retention rate (%) = {longitudinal tensile strength (N/5 cm) after heat-exposure resistance test/longitudinal tensile strength (N/5 cm) before heat-exposure resistance test} × 100.

Example 1

PPS resin

[0073] A 100 mol% linear polyphenylene sulfide resin that was intentionally not copolymerized with trichlorobenzene (made by Toray Industries, Inc., Product No. E2280, MFR: 160 g/10 min) was dried in a nitrogen atmosphere at 160°C for 10 hours, and used in the following procedure.

Spinning and forming into nonwoven web

[0074] The PPS resin was molten in an extruder, and spun from a rectangular spinneret having a hole diameter of 0.50 mm at a spinning temperature of 320°C and at a discharge rate per hole of 1.38 g/min. The spun filamentary streams were allowed to cool down and solidify between the rectangular spinneret and a rectangular ejector at a distance of 55 cm in an atmosphere at room temperature (20°C). The filamentary streams that had cooled down and solidified were passed through the rectangular ejector and were pulled and drawn by compressed air that was heated to 230°C with an air heater and blown out from the ejector at an ejector pressure of 0.15 MPa. The filaments were collected on a moving net to form a nonwoven web.

[0075] The obtained filaments had an average single fiber fineness of 2.8 dtex, a crystallinity of 18.4%, the sum of the rigid amorphous fraction and the crystallinity of 38.2%, and a boiling water shrinkage of 2.3%. The spinning speed was 4,998 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and thermal bonding

[0076] Next, the obtained nonwoven web was temporarily bonded at a linear pressure of 200 N/cm and a temporary bonding temperature of 100°C with a pair of upper and lower metallic calender rolls installed in the production line. The nonwoven fabric was then thermally bonded at a linear pressure of 1000 N/cm and a thermal bonding temperature of 270°C with a roll pair for embossing which provides a bonding area of 12% and which is composed of an upper metallic embossing roll engraved with a polka dot pattern and a lower metallic roll having a flat surface. Thus, a filament nonwoven fabric of Example 1 was obtained.

[0077] The obtained nonwoven fabric had no significant shrinkage in width due to thermal shrinkage by thermal bonding with the embossing roll pair and showed good quality without wrinkles. The obtained filament nonwoven fabric had a mass per unit area of 248 g/m^2, a longitudinal tensile strength of 434 N/5 cm, thermal shrinkage rates of 0.0% in the longitudinal direction and 0.1% in the transverse direction, and a longitudinal tensile strength retention rate of 99%.

Example 2

PPS resin, spinning, and forming into nonwoven web

[0078] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1 except that the temperature of the compressed air was 200°C.

[0079] The obtained filaments had an average single fiber fineness of 2.8 dtex, a crystallinity of 17.3%, the sum of the rigid amorphous fraction and the crystallinity of 37.3%, and a boiling water shrinkage of 7.0%. The spinning speed was 4,991 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and thermal bonding

[0080] Next, the nonwoven web was temporarily bonded and then thermally bonded in the same manner as in Example 1 to produce a filament nonwoven fabric of Example 2.

[0081] The obtained nonwoven fabric had no significant shrinkage in width due to thermal shrinkage by thermal bonding with the embossing roll pair and showed good quality without wrinkles. The obtained filament nonwoven fabric had a mass per unit area of 253 g/m^2, a longitudinal tensile strength of 454 N/5 cm, thermal shrinkage rates of 0.1% in the longitudinal direction and 0.2% in the transverse direction, and a longitudinal tensile strength retention rate of 99%.

Example 3

PPS resin, spinning, and forming into nonwoven web

[0082] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1 except that the temperature of the compressed air was 140°C.

[0083] The obtained filaments had an average single fiber fineness of 2.9 dtex, a crystallinity of 15.1%, the sum of the rigid amorphous fraction and the crystallinity of 31.3%, and a boiling water shrinkage of 17.5%. The spinning speed was 4,824 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and thermal bonding

[0084] Next, the nonwoven web was temporarily bonded and then thermally bonded in the same manner as in Example 1 to produce a filament nonwoven fabric of Example 3.

[0085] The obtained nonwoven fabric had no significant shrinkage in width due to thermal shrinkage by thermal press-bonding with the embossing roll pair and showed good quality without wrinkles. The obtained filament nonwoven fabric had a mass per unit area of 245 a longitudinal tensile strength of 472 N/5 cm, thermal shrinkage rates of 0.0% in the longitudinal direction and 0.1% in the transverse direction, and a longitudinal tensile strength retention rate of 99%.

Example 4

PPS resin, spinning, and forming into nonwoven web

[0086] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in

Example 1 except that the temperature of the compressed air was 200°C and that the ejector pressure was 0.21 MPa.

[0087] The obtained filaments had an average single fiber fineness of 2.4 dtex, a crystallinity of 24.1%, the sum of the rigid amorphous fraction and the crystallinity of 49.2%, and a boiling water shrinkage of 2.2%. The spinning speed was 5,663 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and thermal bonding

[0088] Next, the nonwoven web was temporarily bonded and then thermally bonded in the same manner as in Example 1 to produce a filament nonwoven fabric of Example 4.

[0089] The obtained nonwoven fabric had no significant shrinkage in width due to thermal shrinkage by thermal press-bonding with the embossing roll pair and showed good quality without wrinkles. The obtained filament nonwoven fabric had a mass per unit area of 256 a longitudinal tensile strength of 421 N/5 cm, thermal shrinkage rates of 0.0% in the longitudinal direction and 0.1% in the transverse direction, and a longitudinal tensile strength retention rate of 98%.

Example 5

PPS resin, spinning, and forming into nonwoven web

[0090] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1 except that the temperature of the compressed air was 200°C and that the ejector pressure was 0.25 MPa.

[0091] The obtained filaments had an average single fiber fineness of 2.2 dtex, a crystallinity of 33.0%, the sum of the rigid amorphous fraction and the crystallinity of 67.4%, and a boiling water shrinkage of 2.0%. The spinning speed was 6,198 m/min. In terms of spinnability, during the one-hour spinning, the breakage of the filaments was observed twice.

Temporary bonding and thermal bonding

[0092] Next, the nonwoven web was temporarily bonded and then thermally bonded in the same manner as in Example 1 to produce a filament nonwoven fabric of Example 5.

[0093] The obtained nonwoven fabric had no significant shrinkage in width due to thermal shrinkage by thermal press-bonding with the embossing roll pair and showed good quality without wrinkles. The obtained filament nonwoven fabric had a mass per unit area of 254 a longitudinal tensile strength of 245 N/5 cm, thermal shrinkage rates of 0.0% in the longitudinal direction and 0.1% in the transverse direction, and a longitudinal tensile strength retention rate of 99%.

Example 6

PPS resin, spinning, and forming into nonwoven web

[0094] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1.

Temporary bonding and needle punching

[0095] Next, the nonwoven web was temporarily bonded in the same manner as in Example 1. An oil agent (SM7060: made by Dow Corning Toray Silicone Co., Ltd.) in an amount of 2% by weight relative to the weight of the fibers was applied to the nonwoven web. The nonwoven web was entangled by needle punching at a density of 300 needles/cm^2 with a needle having one barb and a barb depth of 0.06 mm to produce a filament nonwoven fabric of Example 6.

[0096] The obtained filament nonwoven fabric had a mass per unit area of 301 a longitudinal tensile strength of 490 N/5 cm, thermal shrinkage rates of 1.6% in the longitudinal direction and 1.8% in the transverse direction, and a longitudinal tensile strength retention rate of 99%.

Example 7

PPS resin, spinning, and forming into nonwoven web

[0097] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1.

Temporary bonding and water jet punching

[0098] Next, the nonwoven web was temporarily bonded in the same manner as in Example 1. The front and back surfaces of the nonwoven web were alternately entangled at a pressure of 15 MPa with a water jet punching (WJP) machine having nozzles with a diameter of 0.10 mm and a pitch of 0.1 mm. The entangled nonwoven web was dried with a hot air dryer whose temperature was set at 100°C to produce a filament nonwoven fabric of Example 7.

[0099] The obtained filament nonwoven fabric had a mass per unit area of 285 a longitudinal tensile strength of 462 N/5 cm, thermal shrinkage rates of 1.4% in the longitudinal direction and 1.7% in the transverse direction, and a longitudinal tensile strength retention rate of 99%.

Comparative Example 1

PPS resin, spinning, and forming into nonwoven web

[0100] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1 except that the compressed air was at normal temperature (30°C) and that the ejector pressure was 0.15 MPa.

[0101] The obtained filaments had an average single fiber fineness of 3.1 dtex, a crystallinity of 8.9%, the sum of the rigid amorphous fraction and the crystallinity of 10.7%, and a boiling water shrinkage of 61.2%. The spinning speed was 4,435 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and thermal bonding

[0102] Next, temporary bonding and subsequent thermal bonding of the nonwoven web were attempted in the same manner as in Example 1. However, significant shrinkage in width was observed in the nonwoven web due to thermal shrinkage during thermal bonding with the embossing roll pair and the nonwoven web shrunk and hardened, and thus embossing was impossible to perform.

Comparative Example 2

PPS resin, spinning, and forming into nonwoven web

[0103] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1 except that the compressed air was at normal temperature (30°C) and that the ejector pressure was 0.20 MPa.

[0104] The obtained filaments had an average single fiber fineness of 2.6 dtex, a crystallinity of 18.2%, the sum of the rigid amorphous fraction and the crystallinity of 25.3%, and a boiling water shrinkage of 28.5%. The spinning speed was 5,331 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and thermal bonding

[0105] Next, temporary bonding and subsequent thermal bonding of the nonwoven web were attempted in the same manner as in Example 1. However, significant shrinkage in width was observed in the nonwoven web due to thermal shrinkage during thermal bonding with the embossing roll pair and the nonwoven web shrunk and hardened, and thus embossing was impossible to perform.

Comparative Example 3

PPS resin, spinning, and forming into nonwoven web

[0106] The same PPS resin as in Example 1 was spun and formed into a nonwoven web in the same manner as in Example 1 except that the temperature of the compressed air was 230°C and that the ejector pressure was 0.10 MPa.

[0107] The obtained filaments had an average single fiber fineness of 4.9 dtex, a crystallinity of 9.4%, the sum of the rigid amorphous fraction and the crystallinity of 26.8%, and a boiling water shrinkage of 25.0%. The spinning speed was 2,794 m/min. During the one-hour spinning, the occurrence of the breakage of the filaments was zero and thus good spinnability was observed.

Temporary bonding and needle punching

[0108] Next, the nonwoven web was temporarily bonded in the same manner as in Example 1 and then needle punched in the same manner as in Example 6 to produce a filament nonwoven fabric of Comparative Example 3.

[0109] However, the thermal shrinkage rates of the obtained filament nonwoven fabric were significantly high and were 21.2% in the longitudinal direction and 23.4% in the transverse direction. Moreover, the surfaces of the nonwoven fabric after the heat treatment became wrinkled and irregular. The filament nonwoven fabric had a mass per unit area of 295 g/m^2 and a longitudinal tensile strength of 472 N/5 cm. The heat-exposure resistance test could not be performed because of the significant thermal shrinkage.

[0110] The production and processing conditions and the measurement results of the physical properties and the like in the above Examples and Comparative Examples are shown in Table 1.

Table 1

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparable Example 1	Comparable Example 2	Comparable Example 3
PPS resin	MFR	g/10 min	160	160	160	160	160	160	160	160	160	160
Spinning	Spinning temperature	°C	320	320	320	320	320	320	320	320	320	320
	Hole diameter of spinneret	mm	ø0.5	ø0.5	ø0.5	ø0.5	ø0.5	ø0.5	ø0.5	ø0.5	ø0.5	ø0.5
	Discharge rate per spinneret hole	g/min	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
	Temperature of compressed air	°C	230	200	140	200	200	230	230	Normal temperature (30)	Normal temperature (30)	230
	Fineness	dtex	2.8	2.8	2.9	2.4	2.2	2.8	2.8	3.1	2.6	4.9
	Spinning speed	m/min	4998	4991	4824	5663	6198	4998	4998	4435	5331	2794
	Crystallinity	%	18.4	17.3	15.1	24.1	33.0	18.4	18.4	8.9	18.2	9.4
	Mobile amorphous fraction	%	61.8	62.7	68.7	50.8	32.6	61.8	61.8	89.3	74.7	73.2
	Rigid amorphous fraction	%	19.8	20.0	16.2	25.1	34.4	19.8	19.8	1.8	7.1	17.4
	Crystallinity + rigid amorphous fraction	%	38.2	37.3	31.3	49.2	67.4	38.2	38.2	10.7	25.3	26.8
	Boiling water shrinkage	%	2.3	7.0	17.5	2.2	2.0	2.3	2.3	61.2	28.5	25.0
	Number in Figs. 1 and 2	-	(1)	(2)	(3)	(4)	(5)	(1)	(1)	(6)	(7)	(8)
Temporary bonding by calendering	Temperature	°C	100	100	100	100	100	100	100	100	100	100
	Linear pressure	N/cm	200	200	200	200	200	200	200	200	200	200
Thermal bonding	Temperature	°C	270	270	270	270	270	-	-	270	270	-
	Linear pressure	N/cm	1000	1000	1000	1000	1000	-	-	1000	1000	-
Needle punching	Number of needles	need/cm^2	-	-	-	-	-	300	-	-	-	300
Water jet punching	Pressure	MPa	-	-	-	-	-	-	15	-	-	-

(continued)

				Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparable Example 1	Comparable Example 2	Comparable Example 3
Nonwoven fabric	Mass per unit area		g/m^2	248	253	245	256	254	301	285	-	-	295
	Tensile strength (longitudinal)		N/5 cm	434	454	472	421	245	490	462	-	-	472
	Thermal shrinkage rate	Longitudinal	%	0	0.1	0	0	0	1.6	1.4	-	-	21.2
		Transverse	%	0.1	0.2	0.1	0.1	0.1	1.8	1.7	-	-	23.4
	Longitudinal tensile strength retention rate		%	99	99	99	98	99	99	99	-	-	-

[0111] As shown in Table 1, the PPS fibers in Examples 1 to 5 having the sum of the crystallinity and the rigid amorphous fraction of 31.3 to 67.4% could be thermally bonded with the embossing roll pair and moreover thermal shrinkage at 200°C was hardly observed, indicating excellent thermal dimensional stability. Especially, the fibers of Examples 1 to 4 having the crystallinity of 15.1 to 24.1% were excellent in thermal bonding properties and the resulting fabrics had excellent mechanical strength.

[0112] For the filament nonwoven fabrics of Examples 6 and 7 obtained by mechanically entangling the nonwoven web having the sum of the crystallinity and the rigid amorphous fraction of 38.2% by needle punching or water jet punching, thermal shrinkage at 200°C was hardly observed, and the fabrics had excellent thermal dimensional stability.

[0113] In contrast, the fabrics of Comparative Examples 1 and 2 having the sum of the crystallinity and the rigid amorphous fraction of 10.7% and 25.3%, respectively, had high boiling water shrinkage rates. Consequently, significant shrinkage in width was observed in the nonwoven webs due to thermal shrinkage during the thermal bonding and the nonwoven webs shrunk and hardened, and thus embossing was impossible to perform. In Comparative Example 3 in which the nonwoven web had the sum of the crystallinity and the rigid amorphous fraction of 26.8%, the filament nonwoven fabric obtained by mechanical entangling the nonwoven web by needle punching had significant thermal shrinkage at 200°C and was not suitable for practical use.

[0114] The polyphenylene sulfide fiber and the nonwoven fabric comprising the fiber described in the above embodiments and Examples are illustrated to demonstrate the technical ideas of the present invention. The composition of the resin, the spinning and drawing conditions, the nonwoven web forming conditions, the single fiber fineness, the crystallinity, the rigid amorphous fraction, and the like are not limited to those in the above embodiments and Examples and can be modified in various ways within the scope of the claims of the present invention.

[0115] For example, in the above Examples, the case in which a nonwoven web is formed by spun bonding has been described. In the present invention, however, the nonwoven web may be formed by other methods. Needless to say, the type of the PPS resin to be used is not limited to those in the above Examples.

INDUSTRIAL APPLICABILITY

[0116] The nonwoven fabric comprising the polyphenylene sulfide fiber of the present invention has excellent mechanical strength while maintaining the properties of a PPS resin, namely, heat resistance, chemical resistance, and flame retardancy. Therefore, the nonwoven fabric is useful for various industrial applications including heat-resistant filters, electrical insulation materials, and battery separators.

Claims

1. A polyphenylene sulfide fiber comprising polyphenylene sulfide as a main component and having the sum of the crystallinity and the rigid amorphous fraction of 30% to 90%.

2. The polyphenylene sulfide fiber according to claim 1, wherein the crystallinity is not less than 5% and less than 25%.

3. A nonwoven fabric comprising the polyphenylene sulfide fiber according to claim 1 or 2.

4. The nonwoven fabric according to claim 3, which is produced by consolidation by thermal bonding or mechanical entanglement.

Fig. 1

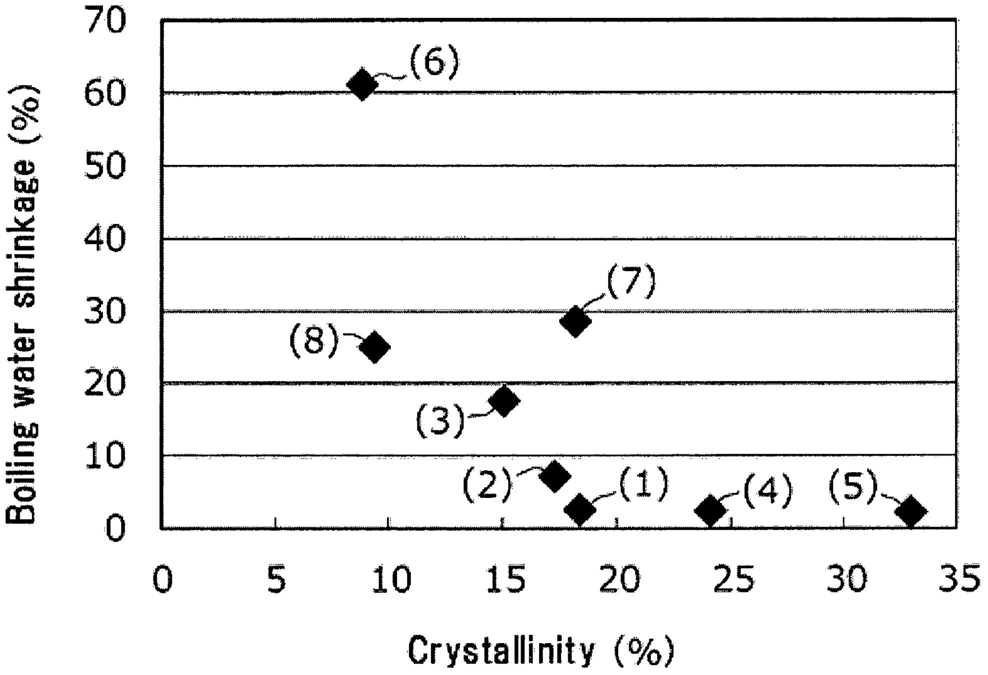
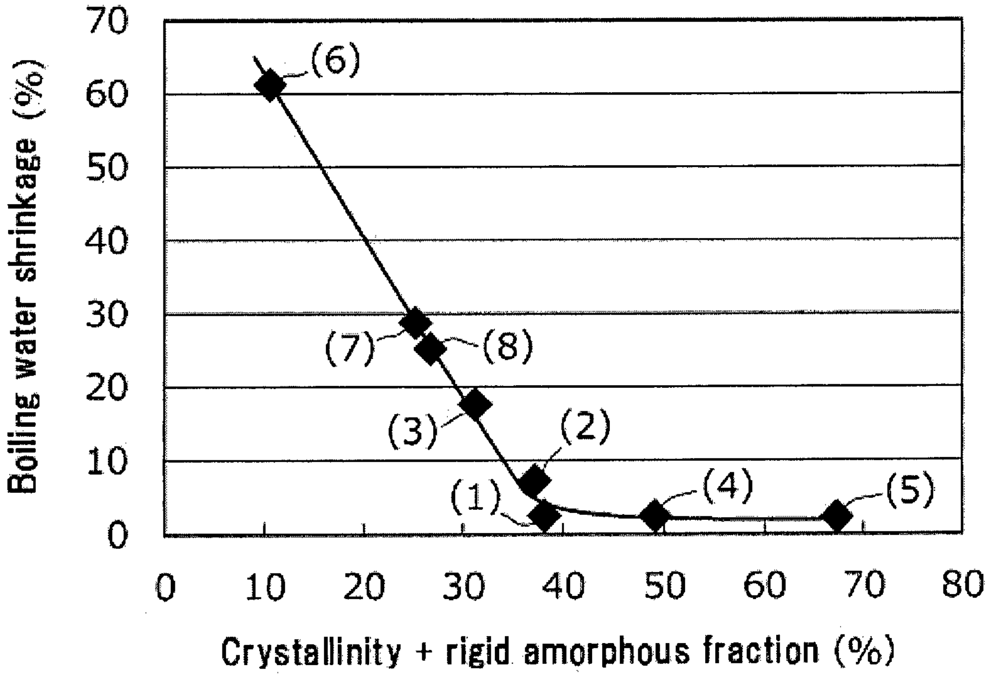

70
60
50
40
30
20
10
0
Boiling water shrinkage (%)
0
5
10
15
20
25
30
35
Crystallinity (%)
(6)
(7)
(8)
(3)
(2)
(1)
(4)
(5)

Fig. 2


70
60
50
40
30
20
10
0
Boiling water shrinkage (%)
0
10
20
30
40
50
60
70
80
Crystallinity + rigid amorphous fraction (%)
(6)
(7)
(8)
(3)
(2)
(1)
(4)
(5)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/064256

A. CLASSIFICATION OF SUBJECT MATTER
D01F6/76(2006.01)i, *D04H3/009*(2012.01)i, *D04H3/08*(2006.01)i, *D04H3/14*(2012.01)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)
D01F6/76, D04H3/009, D04H3/08, D04H3/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580(JDreamII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 2008/035775 A1 (Asahi Kasei Fibers Corp.), 27 March 2008 (27.03.2008), examples 1 to 4 & US 2009/0253329 A1 examples 1 to 4 & JP 4852104 B & EP 2065500 A1 & CN 101512057 A & KR 10-2009-0014297 A	1,3,4 2
X A	WO 2010/110293 A1 (Toray Industries, Inc.), 30 September 2010 (30.09.2010), examples 1 to 4 & US 2011/0298148 A1 examples 1 to 4 & EP 2412857 A1 & CN 102341536 A & KR 10-2011-0128814 A	1,3,4 2

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 07 August, 2012 (07.08.12)	Date of mailing of the international search report 14 August, 2012 (14.08.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/064256

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2011/070999 A1 (Toray Industries, Inc.), 16 June 2011 (16.06.2011), examples 1 to 4 (Family: none)	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2008223209 A **[0006]**
- WO 2008035775 A **[0006]**