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(54) **POLYPHENYLENE SULFIDE COMPOSITE FIBER AND NONWOVEN FABRIC**

(57) A polyphenylene sulfide composite fiber which consists primarily of component A and component B, the component A being a resin primarily containing polyphenylene sulfide made from p-phenylene sulfide as a primary unit, the component B being a resin primarily containing a copolymerized polyphenylene sulfide made from at least one kind of copolymerization unit other than

p-phenylene sulfide, characterized in that at least one part of a fiber surface is made of component B. A thermally adhesive composite fiber and a nonwoven fabric which are made of a resin consisting primarily of polyphenylene sulfide and are excellent in heat resistance, flame retardancy and chemical resistance can be provided.

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DescriptionTechnical Field of the Invention

[0001] The present invention relates to a fiber, which consists primarily of polyphenylene sulfide (may be abbreviated as "PPS") and is excellent in terms of heat resistance and chemical resistance, as well as a nonwoven fabric made from the fiber.

Background Art of the Invention

[0002] The PPS resin has excellent characteristics such as heat resistance, flame retardancy and chemical resistance, and is suitably used as engineer plastic, film, fiber and nonwoven fabric. Above all, the nonwoven fabric is expected to be used for industrial fields of heat-resistant filter, electrical insulating material and battery separator because of its excellent characteristics.

[0003] There have been various suggestions about the nonwoven fabric made from the PPS resin so far. Patent document 1 discloses a long-fiber nonwoven fabric made by thermobonding a fabric which has been spunbonded with the PPS resin and stretched (preferably biaxially stretched) at a temperature higher than the glass transition point. Patent document 2 discloses another long-fiber nonwoven fabric made by thermobonding a fabric which has been spunbonded with the PPS resin to be stretched and temporarily bonded at a temperature lower than the first crystallization temperature and then heat treated at a temperature higher than the first crystallization temperature in a tension state. Patent document 3 discloses a heat-resistant nonwoven fabric integrated by thermobonding a fabric containing 30wt% or more of the PPS resin having a crystallinity of 25 to 50%. However, it has been difficult to make a nonwoven fabric having a high mechanical strength because any of such suggested nonwoven fabrics is constituted by a single fiber component so that it is difficult for fibers to be integrated at the time of thermobonding.

[0004] On the other hand, a thermally adhesive composite fiber which contains a low melting point component for improving a thermal adhesiveness has been known.

[0005] Patent document 4 discloses a long-fiber nonwoven fabric made by thermobonding core-sheath type composite fibers containing the PPS resin as a sheath component and polyethylene terephthalate resin as a core component. However, because the melting point of the sheath component is higher than the core component, such a nonwoven fabric exhibits a thermal adhesiveness just like a fiber made from a single component. Also, the durability is poor because polyethylene terephthalate resin is poor in the flame retardancy and chemical resistance.

[0006] Thus, there has been neither fiber excellent in thermal adhesiveness nor mechanically strong nonwoven fabric as the excellent heat resistance and chemical resistance are derived from the PPS resin.

Prior art documents**Patent documents****[0007]**

Patent document 1: JP2005-154919-A
 Patent document 2: JP2008-223209-A
 Patent document 3: WO2008/035775
 Patent document 4: JP2009-155764-A

Summary of the InventionProblems to be solved by the Invention

[0008] Accordingly, it could be helpful to provide a fiber excellent in thermal adhesiveness as well as a mechanically strong nonwoven fabric while utilizing at maximum the heat resistance, flame retardancy and chemical resistance of the PPS resin.

Means for solving the Problems

[0009] The present invention provides a polyphenylene sulfide composite fiber which consists primarily of component A and component B, the component A being a resin primarily containing polyphenylene sulfide made from p-phenylene sulfide as a primary unit, the component B being a resin primarily containing a copolymerized polyphenylene sulfide

made from at least one kind of copolymerization unit other than p-phenylene sulfide, characterized in that at least one part of a fiber surface is made of component B.

[0010] The present invention even provides a nonwoven fabric made from the polyphenylene sulfide composite fiber.

Effect according to the Invention

[0011] The PPS composite fiber according to the present invention is excellent in a thermal adhesiveness while having characteristics of heat resistance, chemical resistance and flame retardancy of PPS resin. Further, the nonwoven fabric according to the present invention could be used in various industrial fields because of its excellent mechanical strength as well as the characteristics of heat resistance, chemical resistance and flame retardancy of PPS resin.

Embodiments for carrying out the Invention

[0012] It is important for the composite fiber of the present invention to primarily consist of component A and component B, each component containing the PPS primarily. Such configured composite fiber would be excellent in heat resistance, flame retardancy and chemical resistance.

[0013] In the PPS composite fiber of the present invention, it is important that component A which is a resin primarily containing the PPS of which primary unit is p-phenylene sulfide is combined with component B which is a resin primarily containing a copolymerized PPS and which forms at least one part of the fiber surface. Such configured PPS composite fiber would provide a mechanically strong nonwoven fabric in which component B functions as an adhesion component.

[0014] It is preferable that the PPS in component A contains 93mol% or more of the p-phenylene sulfide unit. If the p-phenylene sulfide unit is contained by 93mol% or more (more preferably 95mol% or more), the fiber can be made excellent in spinnability and mechanical strength.

[0015] From viewpoints of heat resistance and chemical resistance, it is preferable that component A contains the PPS resin by 85% by weight, more preferably 90% by weight, and further preferably 95% by weight.

[0016] It is possible that a thermoplastic resin other than the PPS resin is blended with component A as far as inventive effects are not spoiled. The thermoplastic resin other than the PPS resin may be polyetherimide, polyether sulfone, polysulfone, polyphenylene ether, polyester, polyarylate, polyamide, polyamide-imide, polycarbonate, polyolefin, polyetheretherketone or the like.

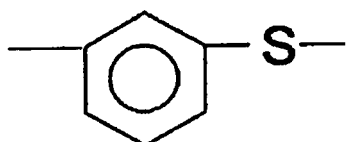
[0017] It is possible that additive such as nucleating agent, delustrant, pigment, mildew-proofing agent, antimicrobial, fire retardant and hydrophilizing agent is added to component A as far as inventive effects are not spoiled.

[0018] It is preferable that a melt flow rate (may be abbreviated as "MFR") according to ASTM D1238-70 (measurement temperature 315.5°C, measurement load 5kg) of component A is 100 to 300 g/10min. If the MFR is 100g/10min or more, and more preferably 140g/10min or more, an appropriate fluidity can suppress the back face pressure of the spinneret from increasing as stretched without the yarn break. On the other hand, if the MFR is 300g/10min or less, and more preferably 225g/10min or less, the polymerization degree or molecular weight can be increased appropriately to achieve a practical mechanical strength and heat resistance.

[0019] The "copolymerized PPS" in component B means what is made by copolymerizing p-phenylene sulfide as a primary repeating unit with at least one other copolymerization unit. It is preferable that the copolymerized PPS contains 70 to 97mol% of p-phenylene sulfide unit among all the repeating units. The p-phenylene sulfide unit, which is contained by 70mol% or more, more preferably 80mol% or more, and further preferably 85mol% or more, would suppress the decrease of the heat resistance. On the other hand, the p-phenylene sulfide unit, which is contained by 97mol% or less, more preferably 96mol% or less, and further preferably 95mol% or less, would provide a composite fiber excellent in thermal adhesiveness.

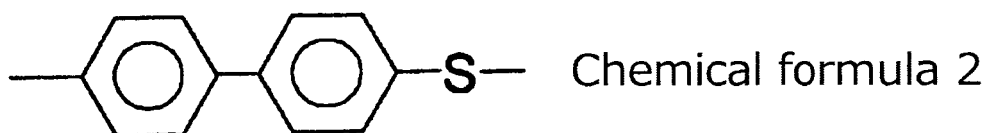
[0020] The copolymerization unit is preferably m-phenylene sulfide unit shown in Chemical formula 1 or others shown in Chemical formulas 2 to 5.

[0021] [Chemical formula 1]

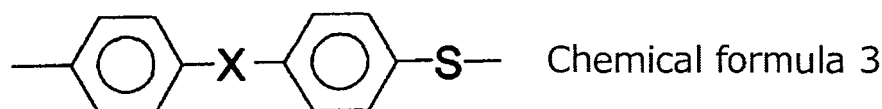


Chemical formula 1

[0022] [Chemical formula 2]

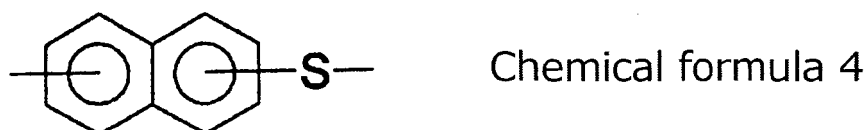


10 [0023] [Chemical formula 3]



15 [0024] (X indicates alkylene, CO, or SO₂ unit.)

[0025] [Chemical formula 4]



25 [0026] [Chemical formula 5]



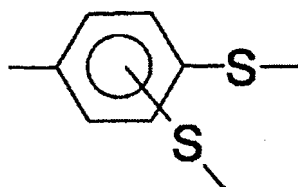
30 [0027] (R indicates alkyl, nitro, phenylene, or alkoxy group.)

[0028] It is possible that it contains several kinds of copolymerization unit other than p-phenylene sulfide. Above all, it is preferable to employ m-phenylene sulfide to make fibers having an excellent spinnability and a desirable melting point with respect to a balance between the thermal adhesiveness and heat resistance.

[0029] It is preferable that the copolymerized PPS has been copolymerized by 5 to 30 mol%. If it is 5mol% or more, more preferably 7mol% or more, and further preferably 9mol% or more, a composite fiber excellent in thermal adhesiveness can be provided. On the other hand, if it is 30mol% or less, more preferably 25mol% or less, and further preferably 20mol% or less, the decrease of the heat resistance can be suppressed.

[0030] Meanwhile, it is preferable that the copolymerized PPS contains 1mol% or less of a trifunctional phenyl sulfide shown in the following Chemical formula representatively so that the fiber is excellent in spinnability.

[Chemical formula 6]



[0031] It is possible that the copolymerized PPS has been subject to random copolymerization, block copolymerization or the like. Above all, it is preferable to employ the random copolymerization to set the melting point to have a good balance of the thermal adhesiveness and heat resistance.

[0032] It is preferable that component B contains the copolymerized PPS by 85% or more by weight, more preferably 90% or more by weight, and further preferably 95% or more by weight, from viewpoints of heat resistance and chemical resistance.

[0033] It is possible that a thermoplastic resin other than the PPS resin is blended with component B as far as inventive effects are not spoiled. The thermoplastic resin other than the PPS resin may be polyetherimide, polyether sulfone, polysulfone, polyphenylene ether, polyester, polyarylate, polyamide, polyamide-imide, polycarbonate, polyolefin, polyetheretherketone or the like.

[0034] It is possible that additive such as nucleating agent, delustrant, pigment, mildew-proofing agent, antimicrobial, fire retardant and hydrophilizing agent is added to component B as far as inventive effects are not spoiled.

[0035] It is preferable that an MFR according to ASTM D1238-70 (measurement temperature 315.5°C, measurement load 5kg) of component B is 100 to 300 g/10min. If the MFR is 100g/10min or more, and more preferably 120g/10min or more, an appropriate fluidity can suppress the back face pressure of the spinneret from increasing as stretched without the yarn break. On the other hand, if the MFR is 300g/10min or less, and more preferably 225g/10min or less, the fluidity can be appropriate enough to form the composite stably.

[0036] It is preferable that the melting point of component B is lower than the melting point of component A because component B is used as a thermal adhesive component.

[0037] The melting point of component B is preferably from 200 to 275°C. If the melting point of the thermal adhesive component is 200°C or higher, more preferably 230°C or higher, and further preferably 240°C or higher, the decrease of the heat resistance can be suppressed. On the other hand, if the melting point of the thermal adhesive component is 275°C or lower, more preferably 270°C or lower, and further preferably 265°C or lower, a composite fiber excellent in thermal adhesiveness can be provided. The melting point of component B can be appropriately controlled based on the molar ratio of components to be copolymerized.

[0038] It is preferable that the difference of melting points between component A and component B is 5 to 80°C. If the difference of melting points is 5°C or higher, more preferably 10°C or higher, and further preferably 15°C or higher, a composite fiber excellent in thermal adhesiveness can be provided. On the other hand, if the difference of melting points is 80°C or lower, more preferably 50°C or lower, and further preferably 40°C or lower, the decrease of the heat resistance can be suppressed.

[0039] It is preferable that the PPS composite fiber contains component B by 5 to 70% by weight. If the content of the second component is 5% or more by weight, more preferably 10% or more by weight, and further preferably 15% or more by weight, the thermobonding can be performed efficiently and firmly. On the other hand, if the content of component B is 70% or less by weight, more preferably 50% or less by weight, and further preferably 30% or less by weight, the decrease of mechanical strength can be suppressed.

[0040] As to the composite form of the PPS composite fiber of the present invention, it is important that component B forms at least one part of a fiber surface. Such a composite form may be of core-sheath type in which round-shaped component A is surrounded by donut-shaped component B concentric in a cross-section of the fiber, core-sheath eccentric type in which the center of component A is out of alignment to the center of component B, sea-island type having sea component A and island component B, parallel type in which both components are in parallel, radial type in which both components are arranged radially by turns, multifoil type in which several components B are arranged around component A or the like. Above all, it is preferable to employ the core-sheath type which contains component B spread all over the fiber surface and is excellent in spinnability of the fiber.

[0041] It is preferable that an average single filament fineness of the PPS composite fiber is 0.5 to 10dtex. If the average single filament fineness is 0.5dtex or more, more preferably 1dtex or more, and further preferably 2dtex or more, the fiber is kept excellent in spinnability and is prevented from frequently breaking at the time of spinning. If the average single filament fineness is 10dtex or less, more preferably 5dtex or less, and further preferably 4dtex or less, the fiber can be cooled sufficiently by suppressing the discharge amount of melted resin per single hole of spinneret, so that the deterioration of spinnability caused by a fusion among fibers is suppressed. In addition, the surface grade can be excellent as the uneven grammage is prevented even when nonwoven fabrics are made. Even from a viewpoint of dust-trapping performance when the nonwoven fabric is used for a filter or the like, the average single filament fineness is preferably 10dtex or less, more preferably 5dtex or less, and further preferably 4dtex or less.

[0042] It is possible that the PPS composite fiber is made from a multifilament, monofilament or short fiber, and is used as a fiber to form fabrics such as woven fabric and nonwoven fabric. Above all, it is preferable that the PPS composite fiber is used as a fiber to form a nonwoven fabric. That is because component fibers thermally adhere to each other so as to enhance the strength of nonwoven fabrics.

[0043] The nonwoven fabric may be needle punched nonwoven fabric, wet nonwoven fabric, spun lace nonwoven fabric, spunbonded nonwoven fabric, meltblown nonwoven fabric, resin-bonded nonwoven fabric, chemical-bonded nonwoven fabric, thermally-bonded nonwoven fabric, tow-opening type nonwoven fabric, air-laid nonwoven fabric or the like. Above all, it is preferable to employ the spunbonded nonwoven fabric excellent in productivity and mechanical strength.

[0044] It is preferable that the nonwoven fabric made from the PPS composite fiber has been integrated by a thermobonding because the thermobonding can increase a mechanical strength.

[0045] It is preferable that a grammage of the nonwoven fabric is 10 to 1,000g/m². If the grammage is 10g/m² or more,

more preferably 100g/m² or more, and further preferably 200g/m² or more, a nonwoven fabric can be provided with a practical mechanical strength. On the other hand, if the grammage is 1,000g/m² or less, more preferably 700g/m² or less, and further preferably 500g/m² or less, the fabric can be provided with an appropriate breathability to suppress a high pressure loss when used for filters or the like.

[0046] In the nonwoven fabric made from thermally adhesive composite fibers according to the present invention, it is preferable that a strength-elongation product per grammage, which is calculated with the following formula from warp tensile strength, warp tensile elongation and grammage of the nonwoven fabric, is 10 or greater.

[0047] Strength-elongation product = warp tensile strength [N/5cm] x warp tensile elongation [%] / grammage [g/m²]

[0048] If the strength-elongation product per grammage is 10 or greater, more preferably 13 or greater and further preferably 15 or greater, the nonwoven fabric can be provided with a mechanical strength enough to be used even under severe environment. Though the upper limit is not prescribed, it is preferable to be 100 or smaller so that the nonwoven fabric is prevented from hardening to deteriorate a handling easiness.

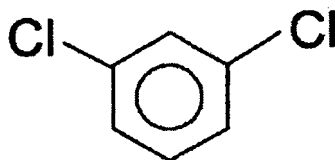
[0049] In the nonwoven fabric made from thermal adhesive composite fibers according to the present invention, it is preferable that a warp tensile strength retention rate in a heat exposure test at 180°C for 1,300 hours is 80% or greater. If the warp tensile strength retention rate is 80% or greater, more preferably 85% or greater and further preferably 90% or greater, the fabric can be used for a heat resistant filter or the like at a high temperature for a long time. Though the upper limit of the warp tensile strength retention rate is not prescribed, it is preferably 150% or smaller.

[0050] Hereinafter, desirable embodiments of a method for manufacturing the PPS composite fiber and a nonwoven fabric according to the present invention will be explained.

[0051] The copolymerized PPS may have been copolymerized by various methods. It is preferable that alkali sulfide, p-dihalobenzene (primary component monomer) and accessory component monomer are mixed according to the above-described molar ratio corresponding to the copolymerization ratio and then are copolymerized in polar solvent in the presence of auxiliary polymerization agent at a high temperature and high pressure, so that the obtained polymer tends to have an increased polymerization degree. Particularly, it is preferable that the alkali sulfide is sodium sulfide, that the primary component monomer is p-dichlorobenzene and that the solvent is N-methylpyrrolidon.

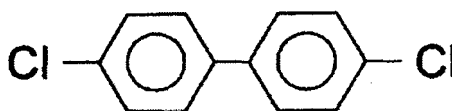
[0052] To introduce m-phenylene sulfide unit shown in Chemical formula 1, the accessory component monomer may be the monomer shown in the following Chemical formula.

[Chemical formula 7]



[0053] To introduce the copolymerization unit shown in Chemical formula 2, it is possible to employ the monomer shown in the following Chemical formula.

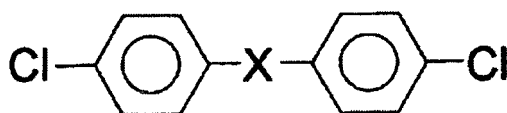
[Chemical formula 8]



[0054] To introduce the copolymerization unit shown in Chemical formula 3, it is possible to employ the monomer shown in the following Chemical formula.

[0055]

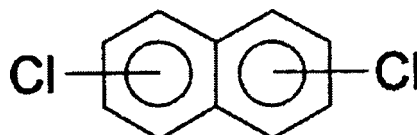
[Chemical formula 9]



[0056] (X indicates alkylene, CO, or SO₂ unit.)

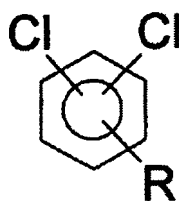
[0057] To introduce the copolymerization unit shown in Chemical formula 4, it is possible to employ the monomer shown in the following Chemical formula.

[Chemical formula 10]



[0058] To introduce the copolymerization unit shown in Chemical formula 5, it is possible to employ the monomer shown in the following Chemical formula.

[Chemical formula 11]



[0059] (R indicates alkyl, nitro, phenylene or alkoxy group.)

[0060] Besides, a plurality of these accessory component monomers may be contained.

[0061] The PPS used in the present invention can be polymerized as well in the polymerization method of the copolymerized PPS except that the accessory component monomer is added by less proportion or is not added.

[0062] The PPS composite fiber of the present invention can be manufactured by a conventional melt spinning method. To manufacture a core-sheath type composite fiber, it is possible that PPS resin as a core component and copolymerized PPS resin as a sheath component are melted with separate extruders and weighed, and then are supplied to a core-sheath type composite spinneret for a melt spinning. After yarns are cooled with a conventional cooling device for lateral or circular blowing, oleum is added and is rolled up on a take-up roller with a rewinder to make a unstretched yarn. To manufacture a short fiber, it is possible that the rolled-up unstretched yarn is stretched with a conventional stretcher on a group of rollers which are different in circumferential speed. After crimped with a push-fit crimper or the like, it may be cut into a desirable length with a cutter such as EC cutter. To manufacture a long fiber, it is possible that after stretched with a stretcher, the fiber is rolled up, and may be subjected to a twisting process or false twisting process if necessary.

[0063] Hereinafter, a method for manufacturing a composite fiber nonwoven fabric by the spunbonding method as a desirable embodiment of a nonwoven fabric of the present invention will be explained.

[0064] The spunbonding method is a manufacturing method to perform a thermobonding, after resin is melted to be spun with a spinneret and then the yarn cooled to solidify is pulled with an ejector and is stretched to gather on a moving net to make an nonwoven web.

[0065] The shapes of spinneret and ejector may be circle, rectangle or the like. Above all, it is preferable to employ the combination of rectangular spinneret and rectangular ejector so that the compressed air consumption is less and yarns do not tend to fusion or scratch to each other.

[0066] It is preferable that a spinning temperature at which the yarn is melted to be spun is 290 to 380°C, more preferably 295 to 360°C, and further preferably 300 to 340°C. If the spinning temperature is in the above-described range, stable melting condition as well as stable spinnability can be exhibited.

[0067] Component A and component B are melted and weighed with separate extruders and then are supplied to a composite spinneret to make a spun composite fiber.

[0068] To cool the spun yarn of the composite fiber, it is possible to employ a method to forcibly blow cool wind toward

the yarn, method to naturally cool the yarn at an atmospheric temperature around the yarn, method to adjust the distance between the spinneret and ejector or combined method of them. The cooling condition may be determined appropriately as considering a discharge rate through a single hole of the spinneret, spinning temperature, atmospheric temperature and the like.

[0069] Next, the yarn cooled to solidify is pulled and stretched with compressed air jetted from an ejector. Though the method and condition of the pulling and stretching with the ejector are not limited in particular, from a viewpoint of efficient crystallization of the PPS fiber, it is preferable to employ a method to pull and stretch the yarn with the compressed air which has been jetted from the ejector and heated to 100°C or higher at a spinning velocity of 3,000m/min or higher. Alternatively, it is preferable to employ a method to pull and stretch the yarn with the compressed air (at normal temperature) of the ejector along a distance adjusted to 450 to 650mm from the bottom face of the spinneret to the compressed air outlet of the ejector at a spinning velocity of 5,000m/min or higher and less than 6,000m/min, from a viewpoint of efficient crystallization of the PPS fiber.

[0070] Next, it is possible that the stretched PPS composite fiber is collected on the moving net to make a nonwoven web, which is integrated by thermobonding to make a nonwoven fabric.

[0071] The thermobonding may be performed as a thermocompression with various rolls, such as top and bottom set of hot embossed rolls having a sculpture on each roll surface, hot embossed rolls consisting of one roll having a flat (smooth) surface and the other roll having a sculpture on its surface, and top and bottom set of hot calender rolls having a flat (smooth) surface on each roll surface. Alternatively, it may be of air-through type to pass hot wind in a thickness direction of the nonwoven web. Above all, it is preferable to employ the thermobonding with the hot embossed rolls so that an appropriate breathability can be maintained while the mechanical strength is improved.

[0072] The shape of the sculpture formed on the embossed roll may be circle, oval, square, rectangle, parallelogram, diamond, regular hexagon, regular octagon or the like.

[0073] It is preferable that the hot embossed roll surface has a temperature between the lower melting point of component B minus 30°C and the lower melting point minus 5°C. If the hot embossed roll surface has a temperature no less than the melting point of component B minus 30°C, more preferably no less than the melting point minus 25°C, and further preferably no less than the melting point minus 20°C, the thermobonding can be performed sufficiently to prevent the nonwoven fabric from exfoliating and becoming fluffy. If the surface has a temperature no more than the melting point minus 5°C, a hole is prevented from generating at a pressure-bonded part by a melting of fibers.

[0074] It is preferable that a linear pressure of the hot embossed roll is 200 to 1,500N/cm at the time of thermobinding. If the linear pressure of the roll is 200N/cm or greater, and more preferably 300N/cm or greater, the thermobonding can be performed sufficiently to prevent the nonwoven fabric from exfoliating and becoming fluffy. On the other hand, if the linear pressure of the roll is 1,500N/cm or smaller, and more preferably 1,000N/cm or smaller, the nonwoven fabric can be prevented from breaking or being bit by a protrusion of the sculpture to make it hard to exfoliate from the roll.

[0075] It is preferable that the contact area on the hot embossed roll is 8 to 40%. If the contact area is 8% or more, more preferably 10% or more, and further preferably 12% or more, the nonwoven fabric can be provided with a practical strength. On the other hand, if the contact area is 40% or less, more preferably 30% or less, and further preferably 20% or less, the nonwoven fabric can be prevented from being like a film without characteristics such as breathability suitable for a nonwoven fabric. When thermobonded with a pair of rolls each having an asperity, the "contact area" means an area proportion of an upper roll salient and a lower roll salient which overlap to contact the nonwoven web in a whole nonwoven fabric. When thermobonded with a roll having an asperity and a flat roll, the "contact area" means an area proportion of the uneven roll salient contacting the nonwoven web in a whole nonwoven fabric.

[0076] To improve a conveyance and to control a thickness of the nonwoven fabric, it is possible that the nonwoven web is temporarily bonded with a calender roll at 70 to 120°C and linear pressure of 50 to 700N/cm before the thermobonding process. The calender rolls may be a set of top and bottom rolls made of metal, or a set of a roll made of metal and another roll made of resin or paper.

[0077] To improve a thermal stability, it is possible to heat-treat a nonwoven web before thermobonded while being tensed with a pin tenter, clip tenter or the like, as well as a tension free heat treatment with a hot wind dryer or the like. It is preferable that the heat treatment is performed at a temperature of the crystallization temperature of the nonwoven web or higher and the melting point of the sheath component or lower.

[Examples]

[0078] Hereinafter, the present invention will be explained specifically based on Examples. The scope of the present invention is not limited to the Examples.

[Measurement method]

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

5 **[0079]** The MFR of the resin is measured according to ASTM D1238-70 at measurement temperature 315.5°C and measurement load 5kg.

(2) Melting point [°C]

10 **[0080]** The measurement is performed with a differential scanning calorimeter (Q100 made by TA Instruments Company) and an average value calculated at the endothermic peak top temperature is determined to be a melting point of the measuring object. When the resin not yet forming a fiber has a plurality of endothermic peaks, the highest peak top temperature is employed. When a fiber is an object to be measured, a melting point of each component can be estimated from a plurality of endothermic peaks measured as well.

15 **[0081]**

- Measurement atmosphere: nitrogen stream (150ml/min)
- Temperature range: 30 to 350°C
- Rate of temperature rise: 20°C/min
- 20 - Sample amount: 5mg

(3) Average single filament fineness [dtex]

25 **[0082]** Ten small pieces are collected randomly from the nonwoven web gathered on a net to photograph a surface image with a microscope by 50 to 1,000 times. Widths of total 100 fibers of 10 per each sample are measured to calculate an average value. The average width of the single filament is regarded as an average diameter of a fiber having a round cross section. The weight per length 10,000m is calculated from a solid density of the resin and is rounded off to one decimal place to determine an average single filament fineness.

30 (4) Spinning velocity [m/min]

[0083] Spinning velocity V [m/min] is calculated based on the following formula from average single filament fineness F [dtex] and discharge of resin discharged through a single hole of the spinneret D [g/min] (may be abbreviated as "single hole discharge D ") predetermined at each condition.

35

$$V = (10,000 \times D) / F$$

(5) Nonwoven fabric grammage [g/m²]

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[0084] According to "6.2 Mass per unit area" in JISL1913 (2010), masses [g] of three 20cm x 25cm pieces per every 1m of sample width are measured to calculate an average mass per unit area [g/m²].

(6) Strength-elongation product per nonwoven fabric grammage

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[0085] According to 6.3.1 in JISL1913 (2010), a sample of size 5cm x 30cm is subject to a tension test for 3 points along warp direction at grip interval 20cm and tensile speed 10cm/min. The strength at the sample breakage is determined as a warp tensile strength [N/5cm] and an elongation measured by 1mm increments at the maximum load relative to the original length is determined as a warp tensile elongation [%]. Each average value of the warp tensile strength [N/5cm] and warp tensile elongation [%] is calculated as rounded off to unit. Next, a strength-elongation product per grammage is calculated from the warp tensile strength [N/5cm], warp tensile elongation [%] and grammage [g/m²] obtained in (5) as rounded off to unit.

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55 Strength-elongation product per grammage = warp tensile strength [N/5cm] x warp tensile elongation [%] / grammage [g/m²]

(7) Nonwoven fabric heat-shrinkage rate [%]

[0086] The measurement is performed according to "5.9 heat-shrinkage rate" in JISL 1906 (2000)". The heat treatment is performed in an isothermal dryer at 200°C for 10 minutes.

(8) Heat exposure test and warp tensile strength retention rate

[0087] Several warp samples of length 30cm x width 5cm are put in a hot wind oven (TABAI SAFETY OVEN SHPS-222 made by Espec company) and is exposed to hot wind air circulating by 300L/min at 180°C for 1,300 hours. A tensile strength of the sample before and after the heat exposure test is measured by the method shown in (6), so as to calculate a warp tensile strength retention rate by the following formula.

$$\text{Warp tensile strength retention rate [\%]} = \frac{\text{warp tensile strength after heat exposure test [N/5cm]}}{\text{warp tensile strength before heat exposure test [N/5cm]}} \times 100$$

[0088] [Example 1]

(Component B)

[0089] 100mol of sodium sulfide nonahydrate, 45mol of sodium acetate and 25 liters of N-methylpyrrolidon (NMP) are mixed in an autoclave and are gradually heated to 220°C while being stirred, and then contained water is distilled away. 91mol (89.8mol%) of p-dichlorobenzene as a primary component monomer, 10mol (10mol%) of m-dichlorobenzene as an accessory component monomer, 0.2mol (0.2mol%) of 1,2,4-trichlorobenzene and 5 liters of NMP are added in the dehydrated system. After nitrogen is filled as pressurized at 3kg/cm² and 170°C, the system is heated so that polymerization is performed at 260°C for 4 hours. After the polymerization, it is cooled so that a polymer is precipitated in distilled water and a small pellet of polymer is collected on a metal net having openings of 150 mesh. Thus obtained small pellet of polymer is washed with distilled water at 90°C for five times and is dried up at 120°C under reduced pressure to make a copolymerized PPS resin having MFR of 152g/10min and melting point of 257°C. The copolymerized PPS resin is dried up in nitrogen atmosphere at 160°C for 10 hours to make component B.

(Component A)

[0090] A PPS resin is prepared as well in the method to make the copolymerized PPS resin, except that 101mol of p-dichlorobenzene is employed as a primary component monomer and neither the accessory component monomer nor 1,2,4-trichlorobenzene is employed. Thus obtained PPS resin has an MFR of 160g/10min and a melting point of 281°C. The PPS resin is dried up in nitrogen atmosphere at 160°C for 10 hours to make component A.

(Spinning / nonwoven web making)

[0091] Component B (copolymerized PPS resin) is melted with an extruder for a sheath component while component A (PPS resin) is melted with an extruder for a core component. Component A and component B are weighed so that the mass ratio is 80:20 and are spun at spinning temperature 325°C and discharged through a rectangular core-sheath type spinneret having pore diameter of φ0.30mm at single hole discharge 1.2g/min. Thus spun and discharged fiber is cooled in an atmosphere at room temperature 20°C to solidify, and then is put through a rectangular ejector placed at a distance of 550mm from the spinneret. Hot air heated to 200°C with an air heater is jetted at ejector pressure 0.17MPa from the ejector, so that the yarn is pulled and stretched to gather on a moving net to make a nonwoven web. Thus obtained core-sheath type composite long fiber has an average single filament fineness of 2.4dtex at a spinning velocity of 5,012m/min while a spinnability is good with 0 yarn breakage during a spinning for one hour.

(Temporary bonding / thermobonding)

[0092] Next, the nonwoven web is temporarily bonded at linear pressure 200N/cm and temporary bonding temperature 90°C with top and bottom set of in-line mounted calender rolls made of metal. Then, the web is thermobonded at linear pressure 1,000N/cm and 250°C with top and bottom set of embossed rolls which have 12% of bonding area and consist of upper roll made of metal having a polka-dotted sculpture and lower flat roll made of metal, so as to make a core-sheath type composite long fiber nonwoven fabric. Thus obtained core-sheath type composite long fiber nonwoven fabric

has a grammage of 256g/m², strength-elongation product per grammage of 20, heat-shrinkage rate of 0.1% in warp direction and 0.1% in weft direction, and warp tensile strength retention rate of 99%.

[Example 2]

(Component B)

[0093] The same copolymerized PPS resin as Example 1 is employed as component B.

(Component A)

[0094] The same PPS resin as Example 1 is employed as component A.

(Spinning / nonwoven web making)

[0095] A core-sheath type composite is spun to make a nonwoven web in the same way as Example 1 except that the compressed air temperature is 20°C (normal temperature) and the ejector pressure is 0.25MPa. Thus obtained core-sheath type composite long fiber has an average single filament fineness of 2.3dtex at a spinning velocity of 5,250m/min while a spinnability is good with 0 yarn breakage during a spinning for one hour.

(Temporary bonding / thermobonding)

[0096] Next, the nonwoven web is temporarily bonded and thermobonded in the same way as Example 1 to make a core-sheath type composite long fiber nonwoven fabric. Thus obtained core-sheath type composite long fiber nonwoven fabric has a grammage of 263g/m², strength-elongation product per grammage of 15, heat-shrinkage rate of 0.1% in warp direction and 0.0% in weft direction, and warp tensile strength retention rate of 98%.

[Example 3]

(Component B)

[0097] A copolymerized PPS resin having MFR of 142g/10min and melting point of 263°C is obtained by the same polymerization method as Example 1, except that 94.8mol (94.8mol%) of p-dichlorobenzene, 5mol (5mol%) of m-dichlorobenzene and 0.2mol (0.2mol%) of 1,2,4-trichlorobenzene are added. Thus obtained copolymerized PPS resin is dried up as well in Example 1 to make component B.

(Component A)

[0098] The same PPS resin as Example 1 is employed as component A.

(Spinning / nonwoven web making)

[0099] A core-sheath type composite is spun to make a nonwoven web from components A and B in the same way as Example 1. Thus obtained core-sheath type composite long fiber has an average single filament fineness of 2.5dtex at a spinning velocity of 4,856m/min while a spinnability is good with 0 yarn breakage during a spinning for one hour.

(Temporary bonding / thermobonding)

[0100] Next, the nonwoven web is temporarily bonded and thermobonded in the same way as Example 1 except that the thermobonding temperature of the embossed roll is 255°C to make a core-sheath type composite long fiber nonwoven fabric. Thus obtained core-sheath type composite long fiber nonwoven fabric has a grammage of 258g/m², strength-elongation product per grammage of 11, heat-shrinkage rate of 0.1% in warp direction and 0.0% in weft direction, and warp tensile strength retention rate of 99%.

[Example 4]

(Component B)

5 **[0101]** A copolymerized PPS resin having MFR of 165g/10min and melting point of 239°C is obtained by the same polymerization method as Example 1, except that 84.8mol (84.8mol%) of p-dichlorobenzene, 15mol (15mol%) of m-dichlorobenzene and 0.2mol (0.2mol%) of 1,2,4-trichlorobenzene are added. Thus obtained copolymerized PPS resin is dried up as well in Example 1 to make component B.

10 (Component A)

[0102] The same PPS resin as Example 1 is employed as component A.

(Spinning / nonwoven web making)

15 **[0103]** A core-sheath type composite is spun to make a nonwoven web from components A and B in the same way as Example 1. Thus obtained core-sheath type composite long fiber has an average single filament fineness of 2.4dtex at a spinning velocity of 5,062m/min while a spinnability is good with 0 yarn breakage during a spinning for one hour.

20 (Temporary bonding / thermobonding)

[0104] Next, the nonwoven web is temporarily bonded and thermobonded in the same way as Example 1 except that the thermobonding temperature of the embossed roll is 230°C to make a core-sheath type composite long fiber nonwoven fabric. Thus obtained core-sheath type composite long fiber nonwoven fabric has a grammage of 255g/m², strength-elongation product per grammage of 19, heat-shrinkage rate of 0.2% in warp direction and 0.1% in weft direction, and warp tensile strength retention rate of 98%.

[Comparative Example 1]

30 (Component B)

[0105] Component B is not added.

(Component A)

35 **[0106]** The same PPS resin as Example 1 is employed as component A.

(Spinning / nonwoven web making)

40 **[0107]** Component A is melted with an extruder to be weighed and spun at spinning temperature 325°C and discharged through a rectangular core-sheath type spinneret having pore diameter of ϕ 0.30mm at single hole discharge 1.2g/min. Then, the spinning is performed to make a nonwoven web in the same way as Example 1. Thus obtained single component type long fiber has an average single filament fineness of 2.4dtex at a spinning velocity of 4,920m/min while a spinnability is good with 0 yarn breakage during a spinning for one hour.

45 (Temporary bonding / thermobonding)

[0108] Next, the nonwoven web is temporarily bonded and thermobonded in the same way as Example 1 except that the thermobonding temperature of the embossed roll is 260°C to make a single component type long fiber nonwoven fabric. Thus obtained single component type long fiber nonwoven fabric has a grammage of 263g/m², strength-elongation product per grammage of 4, heat-shrinkage rate of 0.0% in warp direction and 0.1% in weft direction, and warp tensile strength retention rate of 99%.

[Comparative Example 2]

55 (Component B)

[0109] Component B is not added.

(Component A)

[0110] The same PPS resin as Example 1 is employed as component A.

5 (Spinning / nonwoven web making)

[0111] Component A is melted with an extruder to be weighed and spun at spinning temperature 325°C and discharged through a rectangular single component type spinneret having pore diameter of $\phi 0.30\text{mm}$ at single hole discharge 1.2g/min. Then, the spinning is performed to make a nonwoven web in the same way as Example 1 except that the compressed air temperature is 20°C (normal temperature) and the ejector pressure is 0.25MPa. Thus obtained single component type long fiber has an average single filament fineness of 2.0dtex at a spinning velocity of 5,935m/min while a spinnability is good with 0 yarn breakage during a spinning for one hour.

15 (Temporary bonding / thermobonding)

[0112] Next, the nonwoven web is temporarily bonded and thermobonded in the same way as Example 1 except that the thermobonding temperature of the embossed roll is 260°C to make a single component type long fiber nonwoven fabric. Thus obtained single component type long fiber nonwoven fabric has a grammage of 266g/m², strength-elongation product per grammage of 3, heat-shrinkage rate of 0.1% in warp direction and 0.1% in weft direction, and warp tensile strength retention rate of 99%.

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[Table 1]

		Unit	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Resin	Constituent A	-	PPS	PPS	PPS	PPS	PPS	PPS
		Melting point	281	281	281	281	281	281
		MFR	160	160	160	160	160	160
	Constituent B	-	Copolymerized PPS	Copolymerized PPS	Copolymerized PPS	Copolymerized PPS	None	None
		Copolymerization molar ratio	10	10	5	15		
		Melting point	257	257	263	239		
		MFR	152	152	142	165		
	Complex form		Core/sheath	Core/sheath	Core/sheath	Core/sheath	Single constituent	Single constituent
	Mass ratio [constituent A: constituent B]		80:20	80:20	80:20	80:20	100:0	100:0
	Spinning temperature		325	325	325	325	325	325
Spinning	Spinneret diameter		φ 0.30	φ 0.30	φ 0.30	φ 0.30	φ 0.30	φ 0.30
	Single spinneret discharge rate		1.2	1.2	1.2	1.2	1.2	1.2
	Compressed air temperature		200	normal temp. (20)	200	200	200	normal temp. (20)
	Ejector pressure		0.17	0.25	0.17	0.17	0.17	0.25
	Single yarn average fineness		2.4	2.3	2.5	2.4	2.4	2.0
	Spinning velocity		5,012	5,250	4,856	5,062	4,920	5,935
	Temperature		90	90	90	90	90	90
Temporary adhesion	Linear pressure		200	200	200	200	200	200

(continued)

		Unit	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2
Thermal adhesion	Temperature	°C	250	250	255	230	260	260
	Linear pressure	N/cm	1000	1000	1000	1000	1000	1000
Nonwoven fabric	Grammage	g/m ²	256	263	258	255	263	266
	Strength-elongation product per grammage	-	20	15	11	19	4	3
	Heat-shrinkage rate	%	0.1	0.1	0.1	0.2	0.0	0.1
	Warp	%	0.1	0.0	0.0	0.1	0.1	0.1
	Weft	%	99	98	99	98	99	99
	Warp tensile strength retention rate	%						

[0113] The core-sheath type composite long fiber nonwoven fabrics made from PPS resin primarily consisting of p-phenylene sulfide unit as a core component and copolymerized PPS resin as a sheath component shown in Examples 1 to 4 are excellent in a mechanical strength and have been greatly improved in the strength-elongation product per grammage comparatively from the single component type long fiber nonwoven fabrics shown in Comparative Examples 1 and 2.

Industrial Applications of the Invention

[0114] The nonwoven fabric made from the thermally adhesive composite fiber according to the present invention has characteristics derived from PPS resin, such as heat resistance, chemical resistance and flame retardancy and is excellent in a mechanical strength, and therefore is suitably used for various industrial filters, electric insulating materials, battery separators, film base materials for water treatment, insulating base materials, hazmat suits or the like.

Claims

1. A polyphenylene sulfide composite fiber consisting primarily of component A and component B, wherein the component A is a resin primarily containing polyphenylene sulfide made from p-phenylene sulfide as a primary unit while the component B is a resin primarily containing a copolymerized polyphenylene sulfide made from at least one kind of copolymerization unit other than p-phenylene sulfide, **characterized in that** at least one part of a fiber surface is made of the component B.
2. The polyphenylene sulfide composite fiber according to claim 1, wherein the component A is a core component of a core-sheath type composite fiber while the component B is a sheath component thereof.
3. The polyphenylene sulfide composite fiber according to claim 1 or 2, wherein the component B contains the copolymerized polyphenylene sulfide of which repeating unit has 70 to 97mol% of p-phenylene sulfide and 3 to 30mol% of m-phenylene sulfide.
4. The polyphenylene sulfide composite fiber according to any of claims 1 to 3, wherein melting point T_m (A) of the component A and melting point T_m (B) of the component B satisfy the following formula.

$$5 \text{ [}^\circ\text{C]} \leq T_m \text{ (A)} - T_m \text{ (B)} \leq 80 \text{ [}^\circ\text{C]}$$

5. A nonwoven fabric which has been made from the polyphenylene sulfide composite fiber according to any of claims 1 to 4.
6. The nonwoven fabric according to claim 5, wherein the nonwoven fabric is a spunbonded nonwoven fabric.
7. The nonwoven fabric according to claim 5 or 6, wherein the polyphenylene sulfide composite fiber has been integrated by a thermobonding.
8. The nonwoven fabric according to any of claims 5 to 7, wherein a warp tensile strength retention rate in a heat exposure test at 180°C for 1,300 hours is 80% or greater.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/054906

A. CLASSIFICATION OF SUBJECT MATTER

D01F8/16(2006.01) i, D04H3/009(2012.01) i, D04H3/147(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)

D01F8/00-8/18, D04H1/00-18/04

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2-99614 A (Teijin Ltd.), 11 April 1990 (11.04.1990), claims (Family: none)	1-8
A	JP 4-343712 A (Toray Industries, Inc.), 30 November 1992 (30.11.1992), claims (Family: none)	1-8

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

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
04 April, 2012 (04.04.12)Date of mailing of the international search report
17 April, 2012 (17.04.12)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/054906

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-513270 A (Ticona L.L.C.), 24 May 2007 (24.05.2007), claims & WO 2005/056895 A1 claims & US 2005/0123750 A1 & EP 1689919 A1 & DE 602004013039 D & CN 1890415 A & AT 391798 T	1-8
A	JP 2009-155764 A (Toyobo Co., Ltd.), 16 July 2009 (16.07.2009), claims; paragraph [0038] (Family: none)	1-8

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 2005154919 A [0007]
- JP 2008223209 A [0007]
- WO 2008035775 A [0007]
- JP 2009155764 A [0007]