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(54) POLYVINYL ALCOHOL-BASED FIBER, FIBER STRUCTURE, AND METHOD FOR PRODUCING SAME

(57) [Problem to be solved] a polyvinyl alcohol fiber that have sufficient shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher, especially around 35°C is provided.

[Solution] the present invention relates to a polyvinyl alcohol fiber containing modified polyvinyl alcohol containing 1 mol% or more of a carboxyl group and having a birefringence index of 0.040 or more, a fiber structure using the polyvinyl alcohol fiber, and a method for producing the polyvinyl alcohol fiber.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a polyvinyl alcohol fiber and a fiber structure containing the fiber. Further, the present invention relates to a method for producing a polyvinyl alcohol fiber.

BACKGROUND ART

[0002] Healthcare products such as disposable diapers and incontinence pads and daily necessities such as sanitary napkins or the like play an important role in daily life by absorbing body fluids and maintaining a sense of cleanliness.

[0003] Absorbent articles intended to absorb water such as body fluids generally have a structure in which moisture absorbent is covered with paper or the like, a part of the paper or the like is fixed with hot melt adhesive or the like and the moisture absorbent is provided between a breathable polymer sheet that comes into direct contact with wearer's skin and a water-impermeable nonwoven fabric.

[0004] The moisture absorbent uses a water-absorbing and shrinkable fiber, and when the water-absorbing and shrinkable fiber absorbs water and shrinks, it is possible to prevent liquid leakage by bringing a water absorbing agent into close contact with a human body in addition to ensuring a flow path for moisture to the moisture absorbent.

[0005] As such a water-absorbing and shrinkable fiber, for example, Patent Document 1 discloses a high-speed shrinking fiber comprising modified polyvinyl alcohol containing 0.5 to 10 mol% of a carboxy group, wherein a maximum shrinkage rate of the high-speed shrinking fiber in water at 20°C is 30% or more, a time required to reach 30% shrinkage rate of the high-speed shrinking fiber is 10 seconds or less, a shrinkage stress of the high-speed shrinking fiber in its original length state is 0.15 g/d or more and a time required to develop the shrinkage stress of 0.15 g/d is 10 seconds or less, wherein the high-speed shrinking fiber has the shrinkage stress of 0.03 g/d or more in water at 20°C when shrunk by 30% from its original length, has a dissolution loss of 45% or less when dispersed in water at 20°C and is poorly soluble in water, and wherein the high-speed shrinking fiber shrink in the presence of water.

[0006] Further, Patent Document 2 discloses a water-absorbing and shrinkable polyvinyl alcohol fiber having a shrinkage rate in water of 20 to 50% at 30°C, a ratio of a shrinkage rate in water at 30°C to a maximum shrinkage rate of 0.2 to 0.7 and a wet elastic modulus of 0.1 to 3 cN/dtex, wherein an ash content of the water-absorbing and shrinkable polyvinyl alcohol fiber is 0.2% by mass or less.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0007]

Patent Document 1: JP-A 1987-215011
Patent Document 2: JP-A 2001-262432

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0008] In the above-mentioned applications for healthcare products and daily necessities, the moisture absorbent absorbs water at a temperature around 35°C, which is close to the human body temperature, so for a water-absorbing and shrinkable fiber, a shrinkage rate when absorbing moisture at a temperature of at least room temperature or higher is important.

[0009] Furthermore, since it is necessary to shrink the entire moisture absorbent, the water-absorbing and shrinkable fiber needs to have sufficient shrinkage stress when absorbing moisture at a temperature of at least room temperature or higher.

[0010] In addition, when the moisture absorbent absorbs a large amount of moisture, its shape collapses and breaks due to its own weight, and the absorbent moves between a breathable polymer sheet and nonwoven fabric inside the absorbent article. As a result, the moisture absorbent is unevenly distributed inside the absorbent article, and the absorbent article may not be able to absorb enough moisture, causing leakage.

[0011] In order to prevent such leakage, a water-absorbing and shrinkable fiber is required to have a shrinkage stress that can maintain the shape of the moisture absorbent even after water absorption.

[0012] However, the high-speed shrink fiber disclosed in Patent Document 1 has a dissolution loss of 45% or less when dispersed in water at 20°C, and there is a possibility that the shrinkage stress when absorbing water at a temperature equal to room temperature or higher is insufficient.

[0013] Further, the water-absorbing and shrinkable polyvinyl alcohol fiber disclosed in Patent Document 2 has a shrinkage rate in water of 20 to 50% at 30°C, and it is considered that further improvement in shrinkage rate is necessary.

[0014] Therefore, in order to improve the shrinkage rate and the shrinkage stress, absorbent articles that use a combination of a water-absorbing and shrinkable fiber and a thread rubber are used. However, since the thread rubber is in a shrunk state even before a water absorbent article is used, the absorbent article becomes bulky before use.

[0015] Therefore, there is a need for a shrinkable fiber that have sufficient shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher, particularly around 35°C.

[0016] An object of the present invention is to provide a polyvinyl alcohol fiber that have sufficient shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher, particularly around 35°C. Another object of the present invention is to provide a fiber structure having at least a portion of the above polyvinyl alcohol fiber. Further, another object of the present invention is to provide a method for producing the polyvinyl alcohol fiber.

MEANS FOR SOLVING THE PROBLEM

[0017] That is, the present invention includes the following preferred aspects.

[1] A polyvinyl alcohol fiber comprising modified polyvinyl alcohol containing 1 mol% or more of a carboxy group and having a birefringence index of 0.040 or more.
[2] The polyvinyl alcohol fiber in the above-mentioned item [1], wherein the carboxy group is contained in at least one functional group selected from the group consisting of an acrylic acid group, a methacrylic acid group and an itaconic acid group.
[3] The polyvinyl alcohol fiber in the above-mentioned item [1] or [2], which has a crystallinity of 30 to 60%.
[4] A fiber structure containing at least a portion of the polyvinyl alcohol fiber in any one of the above-mentioned item [1] to [3].
[5] The fiber structure in the above-mentioned item [4], wherein the fiber structure is a nonwoven fabric or a spun yarn.
Further, the present invention includes the following preferred aspects.
[6] A method for producing a polyvinyl alcohol fiber comprising:

> wet or dry-wet spinning a spinning stock solution containing 5 to 30% by mass of modified polyvinyl alcohol containing 1 mol% or more of a carboxy group into a solidifying bath mainly composed of an organic solvent that has a solidifying ability for polyvinyl alcohol,
> wherein in any one step of wet drawing, drying, dry drawing or heat treatment, a total drawing ratio in all steps is set to 7 times or more at 180°C or higher.

[7] The method for producing the polyvinyl alcohol fiber in the above-mentioned item [6], wherein a drawing tension is set to 0.40 cN/dtex or more when the total drawing ratio in all steps is set to 7 times or more.
[8] The method for producing the polyvinyl alcohol fiber in the above-mentioned item [6] or [7], wherein the drawing temperature in the dry drawing step is 180°C or higher.

EFFECTS OF THE INVENTION

[0018] According to the present invention, it is possible to provide a polyvinyl alcohol fiber that have sufficient shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher, especially around 35°C and a fiber structure having at least a portion of the polyvinyl alcohol fiber. Further, it is possible to provide a method for producing the polyvinyl alcohol fiber.

MODE FOR CARRING OUT THE INVENTION

[0019] In the present invention, by using a polyvinyl alcohol fiber that contain modified polyvinyl alcohol containing 1 mol% or more of a carboxy group and have a birefringence index of 0.040 or more (hereinafter also referred to as "present polyvinyl alcohol fiber"), it becomes possible to obtain a water-absorbing and shrinkable fiber that have sufficient shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher, particularly around 35°C.

[0020] Polyvinyl alcohol is obtained by saponifying a vinyl ester polymer obtained by polymerizing vinyl ester monomers. Examples of vinyl ester monomers include vinyl formate, vinyl acetate, vinyl propionate, vinyl valerate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl pivalate, vinyl versatate and the like. Among these, vinyl acetate is preferred.

[0021] The vinyl ester polymer is preferably a polymer using one or more kinds of vinyl ester monomers as a monomer, and more preferably a polymer obtained using one kind of vinyl ester monomer as a monomer. The vinyl ester polymer may be a copolymer of one or more vinyl ester monomers and other monomers copolymerizable therewith.

[0022] Examples of other monomers copolymerizable with the vinyl ester monomer include olefins having 3 to 30 carbon atoms such as propylene, 1-butene, and isobutene; acrylic acid or its salt; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, and octadecyl acrylate; methacrylic acid or its salts; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, i-propyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, and octadecyl methacrylate; acrylamide, N-methylacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, diacetone acrylamide, acrylamide propanesulfonic acid or salts thereof, acrylamidopropyldimethylamine or its salts; acrylamide derivatives such as N-methylolacrylamide or derivatives thereof; methacrylamide derivatives such as methacrylamide, N-methylmethacrylamide, N-ethylmethacrylamide, methacrylamidepropanesulfonic acid or its salts, methacrylamidepropyldimethylamine or its salts, N-methylolmethacrylamide or its derivatives; N-vinyl amides such as N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, i-propyl vinyl ether, n-butyl vinyl ether, i-butyl vinyl ether, t-butyl vinyl ether, dodecyl vinyl ether and stearyl vinyl ether; vinyl cyanides such as acrylonitrile and methacrylonitrile; vinyl halides such as vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride; allyl compounds such as allyl acetate and allyl chloride; maleic acid or its salts, esters or acid anhydrides; itaconic acid or its salts, esters or acid anhydrides; vinylsilyl compounds such as vinyltrimethoxysilane; isopropenyl acetate; and the like. The vinyl ester polymer described above can have a structural unit derived from one or more of these other monomers.

[0023] The modified polyvinyl alcohol containing a carboxy group can be produced by a method of copolymerizing with a monomer containing a carboxy group and saponifying the obtained vinyl ester copolymer when polymerizing the vinyl ester monomer or when copolymerizing the vinyl ester monomer with the other monomer copolymerizable with the vinyl ester monomer as necessary, a method of later introducing these functional groups into pre-synthesized polyvinyl alcohol or the like.

[0024] The carboxy group is preferably contained in a functional group such as an acrylic acid group, a methacrylic acid group or an itaconic acid group, from the viewpoints of stability during copolymerization reaction with vinyl ester and saponification, and the modified polyvinyl alcohol obtained by copolymerizing a monomer containing these functional groups with the vinyl ester monomer is preferred.

[0025] Note that the acrylic acid group refers to a residue obtained by removing hydrogen other than a hydroxy group from acrylic acid and the removed hydrogen is not particularly limited as long as it is other than a hydroxyl group. The same applies to the methacrylic acid group and the itaconic acid group.

[0026] Examples of monomers containing an acrylic acid group as a functional group include acrylic acid or a salt thereof, acrylic esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate and isopropyl acrylate. Among these, acrylic acid and methyl acrylate are preferred from the viewpoints of copolymerization reaction with vinyl ester and stability during saponification.

[0027] Examples of monomers containing methacrylic acid groups include methacrylic acid or its salts, methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate and isopropyl methacrylate. Among them, methacrylic acid and methyl methacrylate are preferred from the viewpoints of copolymerization reaction with vinyl ester and stability during saponification.

[0028] Examples of monomers containing itaconic acid groups include itaconic acid or its salts, itaconic acid esters such as monomethyl itaconate, dimethyl itaconate, monoethyl itaconate, and diethyl itaconate, itaconic anhydride or derivatives thereof. Among them, itaconic acid, monomethyl itaconate and dimethyl itaconate are preferred from the viewpoints of copolymerization reaction with vinyl ester and stability during saponification.

[0029] Among the above monomers, monomers containing at least one functional group selected from the group consisting of acrylic acid groups, methacrylic acid groups and itaconic acid groups are preferred.

[0030] Although one kind or two or more kinds of monomers having these functional groups described above may be used, it is preferable to use one kind of monomer.

[0031] When producing the monomer containing the above functional group and the vinyl ester monomer by copolymerization, by appropriately adjusting an amount of monomers during copolymerization, a content of the carboxy group in the resulting modified polyvinyl alcohol can be adjusted.

[0032] When these functional groups are later introduced into polyvinyl alcohol, the desired functional group content can be achieved by adjusting the amount of the polyvinyl alcohol and the amount of the compound having a functional group.

[0033] Furthermore, the carboxy group in the modified polyvinyl alcohol may be condensed with a hydroxyl group within the molecule or another molecule to form an ester bond within or between molecules or may exist as a metal salt with a metal.

[0034] In the present invention, the content of the carboxy group in the modified polyvinyl alcohol (hereinafter also referred to as "amount of modification") is 1 mol% or more in the modified polyvinyl alcohol from the viewpoint of shrinkage rate when absorbing water at a temperature equal to room temperature or higher and the viewpoint of solubility in water during disposal. The content of the carboxy group is preferably 1.5 mol% or more, and more preferably 2 mol% or more.

[0035] From the viewpoint of shrinkage stress when absorbing moisture at room temperature or higher, the content of the carboxy group is preferably 20 mol% or less, more preferably 6 mol% or less, even more preferably 4 mol% or less, particularly preferably 3 mol% or less.

[0036] Note that the modified polyvinyl alcohol may contain functional groups other than the carboxy group or may be modified with other components as long as the effects of the present invention are not impaired. Other functional groups or components include allylsulfonic acid, vinylpyrrolidone, ethylene and the like.

[0037] A degree of polymerization (viscosity average degree of polymerization) of the modified polyvinyl alcohol is preferably 2400 or less, more preferably 1800 or less from the viewpoints of mechanical strength and suppression of insolubilization due to gelation. If the degree of polymerization is too large, the solubility in water decreases, and disposal of the moisture absorbent after use may become an environmental burden. In addition, from the viewpoints of suppressing deterioration of spinnability and interfiber agglutination and maintaining mechanical performance and quality of fibers and fiber structures, the degree of polymerization is preferably 500 or more, more preferably 700 or more, and particularly preferably 1000 or more.

[0038] The degree of polymerization can be determined by measuring in accordance with JIS K 6726 as described below.

[0039] The present polyvinyl alcohol fiber contains the modified polyvinyl alcohol. The polyvinyl alcohol fiber may contain one kind or two or more kinds of the modified polyvinyl alcohols or may contain the modified polyvinyl alcohol and other polyvinyl alcohols. Furthermore, it may contain other polymers than the polyvinyl alcohol.

[0040] Examples of the present polyvinyl alcohol fiber include:

(a) a polyvinyl alcohol fiber composed of one kind or two or more kinds of the modified polyvinyl alcohols; and
(b) a polyvinyl alcohol fiber composed of the modified polyvinyl alcohol and a polyvinyl alcohol that does not have a carboxy group (hereinafter sometimes referred to as "vinyl alcohol polymer (A)"); and the like. Further, when the present polyvinyl alcohol fiber contains other polymers than polyvinyl alcohol, examples of the present polyvinyl alcohol fiber include:
(c) a polyvinyl alcohol fiber composed of the modified polyvinyl alcohol, the vinyl alcohol polymer (A) and other polymers other than polyvinyl alcohol, or the modified polyvinyl alcohol and other polymers other than polyvinyl alcohol (hereinafter referred to as "other polymers"); and the like.

[0041] In the above-mentioned (a), a plurality of kinds of modified polyvinyl alcohols differ in at least one of the kinds of functional groups containing the carboxy group, the amount of modification, the degree of saponification and the degree of polymerization. Further, in the above-mentioned (b), the degree of saponification and the degree of polymerization of the modified polyvinyl alcohol and the polyvinyl alcohol polymer (A) may be different or the same.

[0042] When the present polyvinyl alcohol fiber contains polyvinyl alcohol other than the modified polyvinyl alcohol or other polymers than polyvinyl alcohol, the content of the modified polyvinyl alcohol in the present polyvinyl alcohol fiber is preferably 70% by mass or more, more preferably 80% by mass or more, and even more preferably 90% by mass or more, based on the total mass of the present polyvinyl alcohol fiber as 100% by mass.

[0043] It is preferable that the polyvinyl alcohol fiber contains 100% by mass of the modified polyvinyl alcohol, and more preferably 100% by mass of one kind of the modified polyvinyl alcohol.

[0044] The polyvinyl alcohol fiber can be produced by spinning these modified polyvinyl alcohols.

[0045] The birefringence index of the present polyvinyl alcohol fiber is 0.040 or more.

[0046] The birefringence index is affected by an orientation state of amorphous and crystalline parts of the polymer, an internal residual stress and the like. When a polyvinyl alcohol fiber having a birefringence index of 0.040 or more absorbs moisture, it is considered that the polyvinyl alcohol fiber exhibits high shrinkage rate and shrinkage stress due to the effects of the orientation state and the residual stress.

[0047] The birefringence index of the present polyvinyl alcohol fiber is preferably 0.041 or more, more preferably 0.042 or more, and even more preferably 0.045 or more.

[0048] The upper limit of the birefringence index is not particularly limited but is usually 0.052 or less.

[0049] The degree of saponification of the present polyvinyl alcohol fiber is preferably 97 mol% or more, more preferably 98 mol% or more, and even more preferably 99 mol% or more. If the degree of saponification is less than the above, the mechanical strength of the polyvinyl alcohol fiber may be poor, and for example, the moisture absorbent may not have sufficient shape retention. Further, if the degree of saponification is less than the above, an elution rate at around 35°C may become high. The higher the degree of saponification is, the higher the shrinkage stress may become. The degree of saponification is usually 100 mol% or less, preferably 99.5 mol% or less.

[0050] As mentioned above, the present polyvinyl alcohol fiber may contain one kind or two or more kinds of modified polyvinyl alcohol. When the present polyvinyl alcohol fiber contains one kind of the modified polyvinyl alcohol, the desired polyvinyl alcohol fiber can be obtained by spinning using the modified polyvinyl alcohol having the degree of saponification within the above range by a method described below.

[0051] When using two or more kinds of the modified polyvinyl alcohol, additivity is established in the degree of saponification of each modified polyvinyl alcohol. Therefore, the degree of saponification of each modified polyvinyl alcohol is determined in advance by measurement or the like, the degree of saponification of the entire polyvinyl alcohol fiber obtained by the following formula (1) may be determined, and the amount of polyvinyl alcohol used may be adjusted so that the obtained degree of saponification falls within the above range.

[0052] The degree of saponification of polyvinyl alcohol can usually be determined by the method described in JIS K 672 6.

$$\text{Saponification degree of polyvinyl alcohol fiber (mol\%)} = [\Sigma(ni \times Mi)]/100 \qquad (1)$$

ni: Saponification degree (mol%) of each modified polyvinyl alcohol
Mi: Ratio of each modified polyvinyl alcohol in polyvinyl alcohol fiber (mass%)

[0053] Note that when the polyvinyl alcohol fiber contains other polymers than the modified polyvinyl alcohol, the ratio of the other polymers than the modified polyvinyl alcohol may be substituted for Mi in the above formula (1). Further, when the other polymer than the modified polyvinyl alcohol is polyvinyl alcohol, the degree of saponification may be substituted for ni, and when the other polymer is other than the polyvinyl alcohol, 0 (zero) may be substituted for ni.

[0054] The crystallinity of the present polyvinyl alcohol fiber is preferably 60% or less, more preferably 50% or less, from the viewpoints of shrinkage characteristics and water solubility. Further, from the viewpoints of shrinkage stress, fiberization and mechanical strength, the crystallinity of the present polyvinyl alcohol fiber is preferably 30% or more, and more preferably 40% or more.

[0055] The degree of crystallinity can be controlled by the degree of polymerization and saponification of the modified polyvinyl alcohol constituting the polyvinyl alcohol fiber, the kind and amount of modification of the functional group containing a carboxy group and the like.

[0056] When producing the polyvinyl alcohol fiber, a spinning stock solution containing the modified polyvinyl alcohol is prepared. A solvent for the spinning stock solution may be water, but it is preferable to use an organic solvent as the solvent for the spinning stock solution since homogeneous fiber with nearly circular cross section having high mechanical performance and dimensional stability is obtained, a fusing temperature in water can be lower than when water is used as the solvent for the spinning stock solution and the organic solvent has excellent water solubility during disposal.

[0057] Examples of organic solvents include polar solvents such as dimethyl sulfoxide (hereinafter also referred to as "DMSO"), dimethylacetamide, dimethylformamide and N-methylpyrrolidone, polyhydric alcohols such as glycerin and ethylene glycol, mixtures of these with swelling metal salts such as rhodan salt, lithium chloride, calcium chloride and zinc chloride, mixtures of these solvents with each other or with water, and the like. In particular, DMSO is most preferred in terms of low-temperature solubility, low toxicity and low corrosivity.

[0058] A concentration of the polyvinyl alcohol in the spinning stock solution is in the range of 5 to 30% by weight. Here, when the polyvinyl alcohol fiber contains only the modified polyvinyl alcohol, the concentration of the polyvinyl alcohol is the concentration of the modified polyvinyl alcohol, and when the polyvinyl alcohol fiber contains the modified polyvinyl alcohol and the vinyl alcohol polymer (A), the concentration is the total concentration of both.

[0059] Note that when the polyvinyl alcohol fiber contains the other polymer, the concentration of the other polymer is not included in the concentration of the polyvinyl alcohol.

[0060] When the solvent of the spinning stock solution is the organic solvent, it is preferable to dissolve these polymers while stirring under reduced pressure after nitrogen substitution, from the viewpoints of preventing oxidation, decomposition, crosslinking reactions and the like and suppressing foaming. The liquid temperature at the time of discharging the spinning stock solution is preferably in the range of 50 to 150°C, within a range that does not cause gelation, decomposition or coloring of the stock solution.

[0061] When the polyvinyl alcohol fiber contains only the modified polyvinyl alcohol, a spinning stock solution of the modified polyvinyl alcohol is prepared using the above solvent. When the polyvinyl alcohol fiber contains the modified polyvinyl alcohol and the vinyl alcohol polymer (A), the modified polyvinyl alcohol and the vinyl alcohol polymer (A) may be mixed in advance and the spinning stock solution may be prepared using the solvent when preparing the spinning stock solution or a solution containing each of the modified polyvinyl alcohol and the vinyl alcohol polymer (A) may be prepared using the above solvent and then each solution may be mixed to form a spinning stock solution.

[0062] When the polyvinyl alcohol fiber further contains the other polymer, either or both of the modified polyvinyl alcohol and the vinyl alcohol polymer (A) may be mixed with other polymers or the other polymer may be dissolved in the solvent in advance.

[0063] A polyvinyl alcohol fiber can be produced by spinning the spinning stock solution prepared as described above. The spinning method is not particularly limited, and examples include a dry spinning method, a wet spinning method and a dry-wet spinning method. Among these, wet spinning or dry-wet spinning is preferred because of its high productivity, and it is sufficient if the fiber is discharged into a solidifying liquid having a solidifying ability for polyvinyl alcohol. In particular, when the spinning stock solution is discharged from multiple holes, the wet spinning method is preferable to the dry-wet spinning method in terms of preventing fibers from sticking to each other during discharge. The wet spinning method is a method in which the spinning stock solution is directly discharged from a spinneret into a solidifying bath, and on the other hand, the dry-wet spinning method is a method in which the spinning stock solution is once discharged from a spinneret into air or an inert gas and then introduced into a solidification bath. In this regard, solidification as used in the present invention refers to a change of the fluid spinning stock solution into a solid with no fluidity and includes both gelation, in which the composition of the stock solution solidifies without changing, and coagulation, in which the composition of the stock solution changes and solidifies.

[0064] When the solvent of the spinning stock solution is water, for example, a saturated aqueous sodium sulfate solution may be discharged as a solidified liquid. When the solvent of the spinning stock solution is an organic solvent, the spinning stock solution may be discharged into the solidification bath mainly containing an organic solvent, for example, such as alcohols such as methanol, ethanol, propanol, butanol, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, fatty acid esters such as methyl acetate, ethyl acetate, aromatics such as benzene, toluene, or mixtures of two or more of these. In order to sufficiently solidify the inside of the fiber, it is preferable to use the solidification bath containing the solvent for the spinning stock solution. A mixing mass ratio of the solvent in the solidification bath/spinning stock solution is preferably from 95/5 to 40/60, more preferably from 90/10 to 50/50, and most preferably from 85/15 to 55/45. Furthermore, by mixing the solvent of the spinning stock solution into the solidification bath, it is possible to adjust the solidification ability and reduce the cost of separating and recovering the solvent of the spinning stock solution and the solidification bath. Although there is no limitation on the temperature of the solidification bath, when the solvent of the spinning stock solution is the organic solvent, the solidification is usually carried out at the solidification bath temperature of -15 to 30°C. From the viewpoints of uniform solidification and energy saving, the solidification bath temperature is preferably -10 to 20°C, more preferably -5 to 15°C, and particularly preferably 0 to 10°C. If the temperature of the solidification bath is outside this temperature range, the tensile strength of the resulting fiber may be reduced. When the spinning stock solution is heated to a high temperature, it is preferable to cool the solidification bath in order to keep the temperature of the solidification bath low.

[0065] Next, wet drawing is applied to the fiber after being removed from the solidification bath, if necessary. From the viewpoints of the mechanical performance of the fiber and prevention of sticking, it is preferable to perform wet drawing at a wet drawing ratio of 1.5 to 5 times, particularly 2.5 to 4 times, and in order to suppress the sticking of threads, it is preferable to increase the wet drawing ratio within a range that does not cause fuzz. In order to increase the wet drawing ratio, it is effective to perform wet drawing by dividing the spinning stock solution into two or more stages during the extraction and removal process, which will be described later.

[0066] In addition, when the solvent of the spinning stock solution is the organic solvent, it is preferable to extract and remove the solvent of the spinning stock solution from the thread by bringing it into contact with an extraction bath mainly composed of an organic solvent having solidification ability. Further, the wet drawing and extraction may be performed in the same process. In this extraction process, a residence time in the extraction bath can be shortened by continuously flowing the pure solidified liquid in a countercurrent direction to the running direction of the string. This extraction process allows the amount of solvent in the spinning stock solution contained in the thread to be 1% or less, particularly 0.1% or less of the weight of the thread, so such a method is preferred. The contact time is preferably 5 seconds or more, particularly 15 seconds or more. In order to increase the extraction rate and improve the extraction, it is preferable to break up the threads in the extraction bath. Further, prior to drying, substituting the solvent of the spinning stock solution with a solvent with a high solidifying ability for polyvinyl alcohol, such as ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, applying hydrophobic oils such as mineral oil, polyethylene oxide, silicone and fluorine in the form of a solution or emulsion, or shrinking to relieve shrinkage stress during drying are also effective in preventing sticking.

[0067] Next, in a drying step, the fiber may be dried preferably at 180°C or lower, and the mechanical performance of the fiber can be improved by further dry drawing. The dry drawing conditions can be appropriately selected depending on the properties of the polyvinyl alcohol, particularly the melting point and desired underwater melting temperature. The dry drawing ratio after the drying step is preferably about 1.1 to 12 times, and the dry drawing temperature is preferably 160 to 220°C. The dry drawing temperature is preferably 160 to 240°C from the viewpoints of process passability and the effect of dry drawing, and particularly preferably 180 to 220°C from the viewpoint of shrinkage rate. From the point of view of efficient drawing while suppressing interfiber agglutination, dry drawing is preferably performed in multiple stages of 6 times or more, and it is particularly preferred to perform multistage stretching at elevated temperatures.

[0068] By performing heat treatment in a heat treatment step after the dry stretching, the degree of crystallinity of the polyvinyl alcohol fiber can be adjusted to a desired range. The temperature of the heat treatment is preferably 160 to 240°C. The heat treatment step and the dry drawing may be performed in the same step.

[0069] In the method for producing a polyvinyl alcohol fiber, in any one step of the wet drawing, drying, dry drawing and heat treatment steps described above, a total drawing ratio in all steps is set to 7 times or more at 180°C or higher. Drawing may be performed such that the total drawing ratio is 7 times or more in any one step of the wet drawing, drying, dry drawing and heat treatment steps.

[0070] Further, a drawing temperature may be 180°C or higher when the total drawing ratio is set to 7 times or more in any one step of the wet drawing, drying, dry drawing and heat treatment steps, and when the total drawing ratio is set to 7 times or more in any one step of the wet drawing, drying, dry drawing and heat treatment steps, it is preferable to set the dry drawing temperature to 180°C or higher from the viewpoint of increasing the birefringence of the resulting polyvinyl alcohol fiber, and it is preferable that the drawing temperature is 180°C or higher and the total drawing ratio is set to 7 times or higher in either the dry drawing or heat treatment step.

[0071] The total drawing ratio is preferably 7 times or more, more preferably 8 times or more, and even more preferably 9 times or more. The upper limit of the total drawing ratio is not particularly limited, but it is preferably within a range that does not cause fluffing of the resulting polyvinyl alcohol fibers and is usually 20 times or less.

[0072] Further, a drawing tension when the total drawing ratio is set to 7 times or more is preferably set to 0.40 cN/dtex or more from the viewpoint of making the birefringence index of the obtained polyvinyl alcohol fiber 0.040 or more and is more preferably set to 0.60 cN/dtex or more from the viewpoint of further increasing the birefringence index. When making the birefringence index of the obtained polyvinyl alcohol fiber 0.040 or more, the drawing tension is a drawing tension when the total drawing ratio in all steps is set to 7 times or more in any one step of the wet stretching, drying, dry stretching, and heat treatment steps. The drawing tension during drawing when the total drawing ratio is not 7 times or more and during drawing after the total drawing ratio is 7 times or more does not necessarily have to be the above-mentioned drawing tension.

[0073] The upper limit of the drawing tension is not particularly limited, but it is preferably within a range that does not cause fluffing of the resulting fiber and is usually 2.0 cN/dtex or less.

[0074] In the method for producing the polyvinyl alcohol fiber of the present invention, the total drawing ratio in all steps is set to 7 times or more at 180°C or higher in any one step of the above wet drawing, drying, dry drawing and heat treatment steps, and the drawing tension is set to 0.40 cN/dtex or more when the total drawing ratio in all steps is set to 7 times or more at 180°C or higher, so that the present polyvinyl alcohol fiber is produced. It is more preferable that the dry drawing temperature is 180°C or higher, and the drawing tension during dry drawing is set to 0.40 cN/dtex or higher.

[0075] That is, the following producing method is mentioned as an example of the method for producing the present polyvinyl alcohol fiber.

[0076] The producing method comprising: wet or dry-wet spinning the spinning stock solution containing 5 to 30% by mass of the modified polyvinyl alcohol containing 1 mol% or more of the carboxy group into the solidifying bath mainly composed of the organic solvent that has a solidifying ability for polyvinyl alcohol, wherein in any one step of wet drawing, drying, dry drawing or heat treatment, the total drawing ratio in all steps is set to 7 times or more at 180°C or higher, and wherein the drawing tension is set to 0.40 cN/dtex or more when the total drawing ratio in all steps is set to 7 times or more at 180°C or higher.

[0077] It is preferable that the polyvinyl alcohol fiber has a high shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher. Therefore, the shrinkage rate of the present polyvinyl alcohol fiber at 35°C is preferably 55% or more, more preferably 60% or more, and even more preferably 65% or more.

[0078] The shrinkage rate and shrinkage stress at 35°C are the shrinkage rate and shrinkage stress when the polyvinyl alcohol fiber absorbs moisture at 35°C, and artificial urine made by adding urea to physiological saline is used as the moisture.

[0079] The shrinkage stress at 35°C is preferably 0.15 cN/dtex or more, more preferably 0.2 cN/dtex or more, and even more preferably 0.23 cN/dtex or more.

[0080] Further, the shrinkage rate of the present polyvinyl alcohol fiber at 45°C is preferably 55% or more, more preferably 60% or more, and even more preferably 65% or more.

[0081] The shrinkage stress at 45°C is preferably 0.15 cN/dtex or more, more preferably 0.2 cN/dtex or more, and even more preferably 0.23 cN/dtex or more.

[0082] The shrinkage rate and shrinkage stress at 45°C are measured in the same manner as in the measurement of the shrinkage rate and shrinkage stress at 35°C, except that the water temperature is set to 45°C.

[0083] The shrinkage rate of the present polyvinyl alcohol fiber at 30 seconds after being immersed in artificial urine at 35°C is preferably 25% or more, more preferably 40% or more from the viewpoints of quickly shrinking when absorbing moisture at a temperature equal to room temperature or higher, especially around 35°C, and securing a moisture flow path.

[0084] From the viewpoint of preventing leakage after moisture absorption, it is preferable that the shrinkage rate is maintained, and the shrinkage rate after 60 seconds of immersion in the artificial urine at 35°C is preferably 30% or more, more preferably 45% or more.

[0085] The shrinkage rate after 300 seconds of immersion in the artificial urine at 35°C is preferably 40% or more, more preferably 55% or more.

[0086] Furthermore, it is preferable that the shrinkage rate for 24 hours after immersion in the artificial urine at 35°C is maintained in the range of 90% to 110% of the shrinkage rate after 300 seconds.

[0087] When the present polyvinyl alcohol fiber is used as a part of the absorbent, it is preferable that the resulting absorbent has excellent water absorption and water retention properties. Therefore, the water absorption ratio of the present polyvinyl alcohol fiber after immersion for 10 minutes is preferably 4 times or more, more preferably 6 times or more. Further, the water absorption ratio after immersion for 1 hour is preferably 5 times or more, more preferably 6 times or more.

[0088] Furthermore, from the viewpoints of water retention and shrinkage stress, the elution rate is preferably 5% or less, more preferably 3% or less.

[0089] The water absorption ratio is a value obtained by immersing the polyvinyl alcohol fiber in physiological saline at 35°C for a certain period of time, measuring the mass of the polyvinyl alcohol fiber after air drying, and dividing the mass before immersion by the mass after immersion, expressed as a percentage. The water absorption ratio after immersion for 1 hour is an absorption ratio when the polyvinyl alcohol fiber is immersed for 1 hour.

[0090] The elution rate is a value obtained by measuring the mass of the polyvinyl alcohol fiber after drying at 120°C for 2.5 hours after measuring the absorption ratio, and dividing the amount of change in mass before and after drying by the mass before drying, expressed as a percentage. Usually, after drying, the mass decreases due to evaporation of water, so the elution rate is the amount of decrease in absorbed water due to drying. Therefore, the smaller the elution rate, the better the water absorption and shrinkage stress.

[0091] When the present polyvinyl alcohol fiber is used for at least a part of a fiber structure described below, from the viewpoint of discarding the fiber structure after use, it is preferable that the present polyvinyl alcohol fiber is water-soluble. Therefore, from the viewpoint of water solubility, the fusing temperature of the present polyvinyl alcohol fiber in water is preferably 80°C or lower, more preferably 60°C or lower.

[0092] There is no particular restriction on the lower limit of the fusing temperature in water, but it may be at room temperature or higher.

[0093] The shrinkage rate, shrinkage stress, absorption rate and elution rate of the present polyvinyl alcohol fiber can be controlled by the amount of modification of the carboxy group, the degree of saponification and the degree of crystallinity of the modified polyvinyl alcohol, and the concentration of the stock solution, the drawing temperature, the heat treatment temperature and the drawing ratio in all steps in the production process of the polyvinyl alcohol fiber.

[0094] A tensile strength of the present polyvinyl alcohol fiber is preferably 3 cN/dtex or more, more preferably 4 cN/dtex or more. Although there is no particular restriction on the upper limit of the tensile strength, it may be 25 cN/dtex or less.

[0095] The tensile strength of the present polyvinyl alcohol fiber can be adjusted to a desired tensile strength by controlling the drawing conditions such as the drawing temperature and the drawing ratio in the method for producing the polyvinyl alcohol fiber.

[0096] Note that other commonly used additives may be added to the present polyvinyl alcohol fiber. An amount of the additive added is preferably 0.1 parts by mass to 10 parts by mass, based on the total mass of the polyvinyl alcohol fiber being 100 parts by mass.

[0097] Although a fineness of the single fiber of the present polyvinyl alcohol fiber is not particularly limited, it can be widely used from about 0.1 to 1000 dtex, particularly from 0.2 to 100 dtex, and more preferably from about 0.5 to 10 dtex. A fiber length of the fiber may be set appropriately depending on the application, but for example, when processing into paper or spun yarn, the fiber length is preferably about 1 to 100 mm. Although there is no limitation on the cross-sectional shape of the polyvinyl alcohol fiber, simple substantially circular fiber is preferable to complex shapes from the viewpoint of water dispersibility and product homogeneity.

[0098] The present polyvinyl alcohol fiber has the excellent shrinkage rate and shrinkage stress when absorbing moisture at a temperature equal to room temperature or higher, especially around 35°C, and the fiber can be used, for example, as moisture absorbents, moisture detection sensors, fishing gear laces, laces for grafting plants, laces for root wrapping, laces for foods, and the like. Among these, it is particularly suitable for use in fiber structures such as moisture absorbents. When used as a moisture absorbent, the fiber can be processed into, for example, filaments, cut fibers, spun yarns, strings, woven or knitted fabrics, non-woven fabrics, ropes, and the like. Among these, non-woven fabrics or spun yarn is preferred. Further, the cut fiber is used with a fiber length of 0.1 to 50 mm, for example.

[0099] When using the present polyvinyl alcohol fiber as a moisture absorbent, the content of the polyvinyl alcohol fiber of the present invention in the moisture absorbent is preferably 30% by mass or more, more preferably 50% by mass or more, and particularly preferably 70 to 100% by mass, based on the total mass of the moisture absorber as 100% by mass.

[0100] Further, as a moisture absorbent, it can be suitably used for sanitary materials, especially liquid-absorbing sanitary materials such as diapers and sanitary products, especially diapers. The form in which the fiber is used is not particularly limited, but remarkable effects can be obtained when the fiber is in the form of strings or non-woven fabrics, and they may also be integrated with other fabrics such as films, woven fabrics, or non-woven fabrics to form products. Furthermore, the present polyvinyl alcohol fiber or the fiber structure using the present polyvinyl alcohol fiber may be used in a part of the product. It is preferable to use the spun yarn or filament form as the string-like material from the viewpoints of exhibiting shrinkage performance, preventing leakage and further improving the fit to the body. For example, by installing a string made of the fiber of the present invention at the end of the diaper, the moisture absorption performance of the diaper can be improved and leakage can be efficiently suppressed.

[0101] In addition to the above-mentioned sanitary materials, the polyvinyl alcohol fiber can be used for moisture detection sensors, fishing gear laces, plant grafting laces, root wrapping laces, food laces, and the like.

[0102] The method for producing the spun yarn is not particularly limited, but it can be produced by any known method for producing the spun yarn, such as ring spinning and tow spinning. In order to effectively develop the water absorption and contraction performance of the present polyvinyl alcohol fiber, the thickness of the spun yarn is preferably about English cotton count No. 1 to No. 20.

[0103] Furthermore, when the present polyvinyl alcohol fiber is used as a dry nonwoven fabric, excellent effects can be obtained in terms of texture, shrinkage performance, suppression of stuffiness and the like. The method for producing the nonwoven fabric is not particularly limited, but examples thereof include a needle punch method and a method of heating a web made by further mixing heat-fusible fibers. In order to effectively develop the water absorption and contraction performance of the polyvinyl alcohol fiber, it is preferable to use a nonwoven fabric produced without using a binder, preferably a needle punched nonwoven fabric. The thickness of the nonwoven fabric is preferably about 0.5 to 3 mm.

[0104] The method for producing such a fabric is not particularly limited, but from the viewpoints of texture, flexibility and the like, it is preferable to use a dry nonwoven fabric obtained by treating a fibrous web. A preferred method for producing the dry nonwoven fabric is, for example, a method in which a web is formed by opening the polyvinyl alcohol fiber filament and the like using a repulsive action of frictional electrification or by opening crimped or cut staples with a card or the like and then this is heat-pressed using a hot embossing roller at an area pressure bonding rate of 10 to 50%, particularly preferably 10 to 30%, that is, 10 to 50%, particularly preferably 10 to 30% of the surface area of the nonwoven fabric. By subjecting a portion of the nonwoven fabric to thermocompression bonding, mechanical performance and morphological stability can be improved without impairing the texture, flexibility, and water solubility of the nonwoven fabric. From the viewpoints of texture, water solubility or the like, the area of each thermocompression bonded part is preferably 4 cm^2 or less, more preferably 2 cm^2 or less, and even more preferably 1 cm^2 or less, and from the viewpoint of mechanical performance of the nonwoven fabric, it is preferably 1 mm^2 or more. The thermocompression bonding temperature may be, for example, about 120 to 230°C, and the pressure may be about 1 to 6 MPa. In addition, since the present polyvinyl alcohol fiber develops adhesive ability through dry heat treatment, such embossing treatment can bond the fibers and efficiently improve the mechanical performance of the nonwoven fabric and it can be easily molded into a desired shape by thermocompression bonding. For example, it may be formed into a desired shape such as a bag shape or a box shape. A bag-shaped material can be suitably used as the packaging material. For example, it may be a bag-like object with a side of about 3 to 10 cm.

[0105] Another method for producing the dry nonwoven fabric includes, for example, a method for producing a nonwoven fabric by performing an interlacing treatment using needle punching. In this case, a dry nonwoven fabric with excellent strength and flexibility can be produced by using a known needle punch machine and adjusting conditions such as needle density, needle type, needle depth, and number of punches according to the properties of the fibers. If needed, entanglement may be optimized through multiple needle punch machines.

EXAMPLES

[0106] Hereinafter, the present invention will be described in more detail below with reference to examples, but the present invention is not limited to these examples in any way.

[0107] The artificial urine and physiological saline used in the following measurements are as follows.

[0108] Artificial urine: Physiological saline with urea added at a concentration of 2% by mass.

[0109] Physiological saline: Phosphate buffered saline with a concentration of 0.01 mol/L.

[Degree of Polymerization]

[0110] Based on JIS K 6726, the degree of polymerization was calculated by the following formula (2) from the measured value of the intrinsic viscosity [η] of an aqueous solution at 30°C. In this regard, P is an average degree of polymerization of the polyvinyl alcohol.

$$\text{Degree of polymerization } P = ([\eta]\times 10^{4}/8.29)^{(1/0.62)} \quad (2)$$

[Degree of Saponification (mol%)]

[0111] Measured according to JIS K 6726-1994.

[Tensile strength (cN/dtex)]

[0112] Measured according to JIS L 1013.

[Birefringence index of polyvinyl alcohol fiber]

[0113] The birefringence index was calculated by using a commercially available polarizing microscope, using a sodium lamp as a light source and determining retardation using the Berek compensator method while the sample was immersed in α-bromnaphthalene.

[Crystallinity of polyvinyl alcohol fiber (%)]

[0114] Using a Mettler differential scanning calorimeter (DSC-20), an endothermic amount ΔH (J/g) at an endothermic peak was measured when 10 mg of the fiber sample was heated at a rate of 20°C/min under nitrogen, and the degree of crystallinity was calculated using the following formula (3) from the ratio to 174.5 J/g, which is the heat of fusion of complete crystals of polyvinyl alcohol.

$$\text{Crystallinity (\%)} = \Delta H\ (\text{J/g})/174.5\ (\text{J/g}) \times 100 \qquad (3)$$

[0115] [Fusing temperature of fiber in water (°C)] (WTb in water)

[0116] A fiber bundle with a length of 10 cm was loaded with a load of 2.2 mg/dtex and suspended in artificial urine at 2°C, and a water temperature was raised at a rate of 2°C/min. A temperature at which the fiber melted and the load dropped was defined as the fusing temperature in water.

[Water absorption ratio of fiber at 35°C]

[0117] The fiber was accurately weighed, immersed in physiological saline at 35°C for 1 hour, left to stand for 10 minutes, drained and weighed. When the mass of the fiber before immersion in the physiological saline is defined as A (g) and the mass after immersion is defined as B (g), the water absorption ratio was calculated using the following formula (4).

$$\text{Water absorption ratio (times)} = (B)/(A) \qquad (4)$$

[Elution rate of fiber (%)]

[0118] The fiber was accurately weighed, immersed in physiological saline at 35°C for 1 hour, left to drain for 10 minutes, dried at 105°C for 4 hours, and then the mass thereof was measured. When the mass of the fiber before immersion in physiological saline is defined as A (g), and the mass after immersion and drying is defined as C (g), the elution rate was calculated using the following formula (5).

$$\text{Elution rate (\%)} = [(A)-(C)]/(A) \times 100 \qquad (5)$$

[Shrinkage rate of fiber at 35°C (%)]

[0119] A fiber bundle with a length of 10 cm was suspended in artificial urine at 2°C with a load of 2.2 mg/dtex, and the water temperature was raised at a rate of 2°C/min. And then, the shrinkage rate at 35°C was calculated by dividing the length of the fiber at 35°C by the original length before the fiber melted and the load dropped.

[Shrinkage stress of fiber at 35°C (cN/dtex)]

[0120] Using a hand-tight chuck for A cell, a 10 cm long fiber bundle was fixed at both ends with an initial load of 1/10 g/dtex, immersed in a water bath and heated at a rate of 0.9°C/min. And then the stress was measured at 35°C using an Autograph-AG-IS/I/IC/EZGraph.

[Shrinkage stress of fiber at 45°C (cN/dtex)]

[0121] Using a hand-tight chuck for A cell, a 10 cm long fiber bundle was fixed at both ends with an initial load of 1/10 g/dtex, immersed in a water bath and heated at a rate of 0.9°C/min. And then the stress was measured at 45°C using an

Autograph-AG-IS/I/IC/EZGraph.

[Shrinkage rate of fiber after 30 seconds (%)]

[0122] A fiber bundle with a length of 10 cm was subjected to a load of 0.15 mg/dtex and suspended in physiological saline at 35°C, and then the shrinkage rate was measured after 30 seconds.

[Shrinkage rate of fiber after 60 seconds (%)]

[0123] A fiber bundle with a length of 10 cm was subjected to a load of 0.15 mg/dtex and suspended in physiological saline at 35°C, and then the shrinkage rate was measured after 60 seconds.

[Shrinkage rate of fiber after 300 seconds (%)]

[0124] A fiber bundle with a length of 10 cm was subjected to a load of 0.15 mg/dtex and suspended in physiological saline at 35°C, and then the shrinkage rate was measured after 300 seconds.

[Shrinkage rate of fiber after 24 hours (%)]

[0125] A fiber bundle with a length of 10 cm was subjected to a load of 0.15 mg/dtex and suspended in physiological saline at 35°C, and then the shrinkage rate was measured after 24 hours.

[Leakproof property of nonwoven fabric sheet]

[0126] A spun yarn with a shrinkage yarn type English cotton count No. 10 was obtained by using known methods such as ring spinning and tow spinning from polyvinyl alcohol fiber yarn. Next, 200 mm of spun yarn was sewn to both ends of the pulp sheet containing 300 g/m^2 of water-absorbing material. Thereafter, 20 g of artificial urine at 35°C was poured onto the pulp sheet and allowed to stand for 1 minute, and the subsequent urine leakage status was evaluated as o if there was no leakage and × if there was leakage.

<Example 1>

[0127] Modified polyvinyl alcohol containing 5.2 mol% of an acrylic group, which is a copolymer with methyl acrylate in which an acrylic acid group contains a carboxy group ("Elvanol 80-18" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 22% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 80/20 at 10°C through a nozzle with a number of holes of 40,000 and a hole diameter of 0.08 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 140°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 3.3 times (total drawing ratio TD = 10 times). The drawing tension at this time was 0.61 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Example 2>

[0128] Modified polyvinyl alcohol containing 2.5 mol% of a methacrylic group, which is a copolymer with methyl methacrylate in which a methacrylic acid group contains a carboxy group ("Elvanol T-25" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 20% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 70/30 at 10°C through a nozzle with a number of holes of 35,000 and a hole diameter of 0.08 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 140°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 3.3 times (total drawing ratio TD = 10 times). The drawing tension at this time was 0.68 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Example 3>

[0129] Modified polyvinyl alcohol containing 2.5 mol% of a methacrylic group, which is a copolymer with methyl methacrylate in which a methacrylic acid group contains a carboxy group ("Elvanol T-25" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 20% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 70/30 at 10°C through a nozzle with a number of holes of 35,000 and a hole diameter of 0.08 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 140°C, and then the resulting dry fiber was subjected to dry heat drawing at 200°C at a dry heat drawing ratio of 4 times (total drawing ratio TD = 12 times). The drawing tension at this time was 1.15 cN/dtex. Then, dry heat shrinkage was performed at 200°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Example 4>

[0130] Modified polyvinyl alcohol containing 1.8 mol% of a methacrylic group, which is a copolymer with methyl methacrylate in which a methacrylic acid group contains a carboxy group ("Elvanol T-66" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 20% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 70/30 at 10°C through a nozzle with a number of holes of 35,000 and a hole diameter of 0.08 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 140°C, and then the resulting dry fiber was subjected to dry heat drawing at 190°C at a dry heat drawing ratio of 3.0 times (total drawing ratio TD = 9 times). The drawing tension at this time was 0.64 cN/dtex. Then, dry heat shrinkage was performed at 190°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Example 5>

[0131] Modified polyvinyl alcohol containing 1.5 mol% of an itaconic acid group, which is a copolymer with itaconic acid in which the itaconic acid group contains a carboxy group ("KL-118" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 19% by mass. This spinning stock solution was dry-wet spun into a solidification bath of methanol/DMSO = 80/20 at 5°C through a nozzle with a number of holes of 80 and a hole diameter of 0.12 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 120°C, and then the resulting dry fiber was subjected to dry heat drawing at 200°C at a dry heat drawing ratio of 3.33 times (total drawing ratio TD - 10.0 times). The drawing tension at this time was 0.69 cN/dtex. Then, dry heat shrinkage was performed at 200°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Example 6>

[0132] Modified polyvinyl alcohol containing 1.8 mol% of a methacrylic group, which is a copolymer with methyl methacrylate in which the methacrylic group contains a carboxy group ("Elvanol T-66" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 20% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 70/30 at 10°C through a nozzle with a number of holes of 35,000 and a hole diameter of 0.08 mmϕ and subjected to 2.5 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 140°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 2.8 times (total drawing ratio TD = 7 times). The drawing tension at this time was 0.43 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Example 7>

[0133] Modified polyvinyl alcohol containing 3.0 mol% of an acrylic group, which is a copolymer with methyl acrylate in which an acrylic acid group contains a carboxy group (degree of polymerization: 1400) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 21% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 80/20 at 5°C through a nozzle with a number of holes of 80 and a hole diameter of 0.12 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 120°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 3.3 times (total drawing ratio TD = 10 times). The drawing tension at this time was 0.75 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Comparative Example 1>

[0134] Modified polyvinyl alcohol containing 5.2 mol% of an acrylic group, which is a copolymer with methyl acrylate in which the acrylic group contains a carboxy group ("Elvanol 80-18" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 22% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 80/20 at 10°C through a nozzle with a number of holes of 40,000 and a hole diameter of 0.08 mmϕ and subjected to 2.5 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 140°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 2.0 times (total drawing ratio TD = 5 times). The drawing tension at this time was 0.31 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Comparative Example 2>

[0135] Polyvinyl alcohol containing no carboxyl group ("27-96" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 21% by mass. This spinning stock solution was wet-spun into a solidification bath of methanol/DMSO = 80/20 at 10°C through a nozzle with a number of holes of 40,000 and a hole diameter of 0.08 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 165°C, and then the resulting dry fiber was subjected to dry heat drawing at 203°C at a dry heat drawing ratio of 2.7 times (total drawing ratio TD = 8.0 times). The drawing tension at this time was 0.40 cN/dtex. Then, dry heat shrinkage was performed at 203°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Comparative Example 3>

[0136] Modified polyvinyl alcohol containing 1.5 mol% of an itaconic acid group, which is a copolymer with itaconic acid in which the itaconic acid group contains a carboxy group ("KL-118" manufactured by Kuraray) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 20% by mass. This spinning stock solution was dry-wet spun into a solidification bath of methanol/DMSO = 80/20 at 5°C through a nozzle with a number of holes of 80 and a hole diameter of 0.12 mmϕ and subjected to 1.5 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 120°C, and then the resulting dry fiber was subjected to dry heat drawing at 190°C at a dry heat drawing ratio of 3.67 times (total drawing ratio TD - 5.5 times). The drawing tension at this time was 0.34 cN/dtex. Then, dry heat shrinkage was performed at 190°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Comparative Example 4>

[0137] Modified polyvinyl alcohol containing 0.5 mol% of a methacrylic group, which is a copolymer with methyl methacrylate in which a methacrylic acid group contains a carboxy group (degree of polymerization: 1600) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 20% by mass. This spinning stock solution was dry-wet spun into a solidification bath of methanol/DMSO = 70/30 at 5°C through a nozzle with a number of holes of 80 and a hole diameter of 0.1 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 120°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 3.3 times (total drawing ratio TD - 10 times). The drawing tension at this time was 0.60 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

<Comparative Example 5>

[0138] Modified polyvinyl alcohol containing 7.0 mol% of a methacrylic group, which is a copolymer with methyl methacrylate in which a methacrylic acid group contains a carboxy group (degree of polymerization: 1600) was dissolved in DMSO with stirring at 90°C for 5 hours to obtain a spinning stock solution having a polyvinyl alcohol concentration of 24% by mass. This spinning stock solution was dry-wet spun into a solidification bath of methanol/DMSO = 80/20 at 5°C through a nozzle with a number of holes of 80 and a hole diameter of 0.12 mmϕ and subjected to 3.0 times wet heat drawing in a methanol bath at 20°C. Next, after extracting the DMSO in a thread with methanol, a spinning oil was applied to the thread and the thread was dried at 120°C, and then the resulting dry fiber was subjected to dry heat drawing at 180°C at a dry heat drawing ratio of 3.3 times (total drawing ratio TD - 10 times). The drawing tension at this time was 0.32 cN/dtex. Then, dry heat shrinkage was performed at 180°C and a dry heat shrinkage rate of 1% to produce a polyvinyl alcohol fiber. Tables 1 and 2 show the results of measuring the birefringence index, crystallinity, fusing temperature in water, water absorption ratio, elution rate, shrinkage rate, shrinkage stress and leakproof property of a nonwoven fabric sheet of the obtained fiber.

[Table 1]

	Monomer for modification	Amount of modifies tion (mol%)	Degree of Saponification (mol%)	Drawing ratio (times)	Drawing tension (cN/dtex.)	Birefringence index	Crystallinity (%)	Fusing temperature in water (°C)	Water absorption ratio at 35°C (times)	Elution rate %
Example 1	Methyl acrylate	5.2	99.5	10	0.61	0.046	47.2	50.2	6.7	2.4
Example 2	Methyl methacrylate	2.5	99.5	10	0.63	0.044	47.4	56.4	6.4	4.2
Example 3	Methyl methacrylate	2.5	99.5	12	1.15	0.046	56.8	59.1	5.4	2.3
Example 4	Methyl methacrylate	1.8	99.5	9	0.64	0.043	43.2	55.5	6.9	4.2
Example 5	Itaconic acid	1.5	97.0	10	0.69	0.041	54.6	60.4	5.4	4.5
Example 6	Methyl methacrylate	1.8	99.5	7	0.43	0.040	46.5	56.1	6.7	4.5
Example 7	Methyl acrylate	3.0	99.5	10	0.75	0.048	47.5	55.2	5.4	2.1
Comparative Example 1	Methyl acrylate	5.2	99.5	5	0.31	0.034	47.1	50.1	8.4	16.5
Comparative Example 2	Unmodified PVA	-	96.5	3	0.40	0.037	45.2	56.4	6.2	2.7
Comparative Example 3	Itaconic acid	1.5	97.0	5.5	0.34	0.037	40.5	50.5	6.2	16.2
Comparative Example 4	Methyl methacrylate	0.5	99.5	10	0.60	0.046	57.0	50.0	3.5	1.5
Comparative Example 5	Methyl methacrylate	7.0	99.5	10	0.32	0.032	39.3	43.5	7.5	5.7

[Table 2]

	Monomer for modification	Shrinkage rate at 35°C (%)	Shrinkage stress at 35°C (cN/dtex)	Shrinkage stress at 45°C (cN/dtex)	Shrinkage rate after 30 seconds (%)	Shrinkage rate after 60 seconds (%)	Shrinkage rate after 300 seconds (%)	Shrinkage rate after 24 hours (%)	Leakproof property of nonwoven fabric sheet
Example 1	Methyl acrylate	74	0.22	0.25	52	74	76	78	○
Example 2	Methyl methacrylate	71	0.20	0.21	49	72	75	73	○
Example 3	Methyl methacrylate	74	0.30	0.30	40	73	75	78	○
Example 4	Methyl methacrylate	69	0.19	0.18	35	65	70	72	○
Example 5	Itaconic acid	70	0.17	0.17	35	65	68	70	○
Example 6	Methyl methacrylate	61	0.16	0.15	25	60	62	65	○
Example 7	Methyl acrylate	71	0.25	0.30	40	71	73	73	○
Comparative Example 1	Methyl acrylate	50	0.05	0.03	20	40	45	fusing	×
Comparative Example 2	Unmodified PVA	51	0.11	0.12	25	36	47	50	×
Comparative Example 3	Itaconic acid	53	0.03	0.02	30	42	50	fusing	×
Comparative Example 4	Methyl methacrylate	15	0.05	0.05	3	5	10	10	×
Comparative Example 5	Methyl methacrylate	45	0.18	0.15	40	40	45	45	×

[0139] As is clear from Tables 1 and 2 above, the present polyvinyl alcohol fiber containing modified polyvinyl alcohol containing 1 mol% or more of a carboxyl group and having a birefringence index of 0.040 or more has excellent shrinkage rate and shrinkage stress at 35°C.

[0140] For example, in the case of the polyvinyl alcohol fibers with a birefringence index of less than 0.040 as shown in Comparative Examples 1, 3 and 5, even if they contain modified polyvinyl alcohol containing 1 mol% or more of a carboxyl group, the shrinkage rate and shrinkage stress are low, and the leakproof property when made into a nonwoven fabric is poor. In addition, the elution rate is high and the shrinkage stress is poor in practical use.

[0141] In Comparative Example 2, which is the polyvinyl alcohol fiber that has a birefringence index of less than 0.040 and does not contain modified polyvinyl alcohol containing a carboxy group, the shrinkage rate and shrinkage stress were low, and the leakproof property when made into a nonwoven fabric was poor.

[0142] In Comparative Example 4, which is the polyvinyl alcohol fiber containing modified polyvinyl alcohol having a carboxy group content of less than 1 mol%, even if the birefringence index was 0.040 or more, the shrinkage rate and shrinkage stress were low, and the leakproof property when made into a nonwoven fabric was poor.

[0143] Therefore, by using the present polyvinyl alcohol fiber in a moisture absorbent, it is possible to secure a moisture flow path and prevent liquid leakage when moisture is absorbed at room temperature or higher, particularly around 35°C.

Claims

1. A polyvinyl alcohol fiber comprising modified polyvinyl alcohol containing 1 mol% or more of a carboxy group and having a birefringence index of 0.040 or more.

2. The polyvinyl alcohol fiber as claimed in claim 1, wherein the carboxy group is contained in at least one functional group selected from the group consisting of an acrylic acid group, a methacrylic acid group and an itaconic acid group.

3. The polyvinyl alcohol fiber as claimed in claim 1 or 2, which has a crystallinity of 30 to 60%.

4. A fiber structure containing at least a portion of the polyvinyl alcohol fiber as claimed in any one of claims 1 to 3.

5. The fiber structure as claimed in claim 4, wherein the fiber structure is a nonwoven fabric or a spun yarn.

6. A method for producing a polyvinyl alcohol fiber comprising:

   wet or dry-wet spinning a spinning stock solution containing 5 to 30% by mass of modified polyvinyl alcohol containing 1 mol% or more of a carboxy group into a solidifying bath mainly composed of an organic solvent that has a solidifying ability for polyvinyl alcohol,
   wherein in any one step of wet drawing, drying, dry drawing or heat treatment, a total drawing ratio in all steps is set to 7 times or more at 180°C or higher.

7. The method for producing the polyvinyl alcohol fiber as claimed in claim 6, wherein a drawing tension is set to 0.40 cN/dtex or more when the total drawing ratio in all steps is set to 7 times or more.

8. The method for producing the polyvinyl alcohol fiber as claimed in claim 6 or 7, wherein the drawing temperature in the dry drawing step is 180°C or higher.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/34(2006.01)i
FI: D01F6/34 Z

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D01F1/00-6/96

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2004-293022 A (KURARAY CO LTD) 21 October 2004 (2004-10-21) claims 1, 5, paragraphs [0014], [0015], [0023]-[0033], [0063], examples	1-8
Y	JP 1-168912 A (NICHIBI KK) 04 July 1989 (1989-07-04) claims, p. 1, right column, line 15 to p. 2, upper left column, line 1, p. 2, upper left column, lines 6-8, p. 3, upper right column, lines 11-15, p. 5, lower right column, line 3 from the bottom to p. 6, line 2	1-5
Y	JP 3-193910 A (TORAY IND INC) 23 August 1991 (1991-08-23) claims 1, 2, p. 1, right column, lines 12-18, p. 3, upper left column, lines 11-13, p. 3, upper left column, lines 16-19, p. 3, lower right column, lines 4-12, p. 5, lower right column, lines 12-16, examples	1-8
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Y	JP 2021-017659 A (KURARAY CO LTD) 15 February 2021 (2021-02-15) paragraph [0019]	3
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☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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International application No.
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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- JP 2001262432 A **[0007]**