Fibrillatable fiber of a sea-islands structure

Fibrillierbare Faser mit 'Inseln-See' Struktur

Fibre fibrillable à structure 'îles-dans-la-mer'

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Description

[0001] The present invention relates to a readily fibrillatable fiber comprising a vinyl alcohol polymer (abbreviated as “PVA” hereinafter) and a vinyl polymer different from the PVA. Preferably an acrylonitrile polymer (abbreviated as “PAN” hereinbelow), characterized in that the fiber is readily modified into a super-fine fibril through the single action of chemically expanding force or mechanical stress or the combination thereof and is therefore preferable for use in wet-type or dry-type non-woven fabric, friction material and reinforcing fiber for cement and rubber.

[0002] As the reinforcing fiber of a variety of friction materials for use in automobile brakes and clutch plates, conventionally, use has been made of asbestos, frequently, in view of the trapping performance of inorganic micro-particles: thermal resistance, heat fusion resistance, reinforcing properties and the like. However, the use of asbestos has been put under strict regulations because of concern that asbestos may be harmful for human health. In recent years, therefore, the fibril of costly aramide fiber has been selected as an alternative thereof. However, aramide fiber is so costly that it is also used in a limited fashion. Thus, materials with insufficient reinforcing performance, such as natural pulp, are used as a kind of filler in combination, but such filler materials deteriorate the performance of the resulting products. Hence, a readily fibrillatable fiber has been desired, which is less expensive than aramide fiber and which has fibrillating properties so as to procure particle trapping performance, heat fusion resistance and reinforcing properties in combination.

[0003] Because asbestos is now under very strict regulations for the reason described above also in the field of slate plates and the like where asbestos has been used for reinforcing cement, general-purpose fibers such as vinylon are therefore currently used as an alternative to asbestos. Because general-purpose fibers are of a larger size than the size of asbestos, the resulting reinforced slate has such a lower green strength that the slate should be mixed with the fibril of natural pulp. These thick fibers and natural pulp deteriorate the product performance. Thus, the development of a fibrillatable fiber of a greater strength has been demanded. For reinforcing rubber and the like, meta- or para-aramide fiber or vinylon has been used, but such fiber is also problematic in that the fiber should be treated with resorcin-formaldehyde-latex process so as to enhance the adhesivity. Hence, a readily fibrillatable fiber of a higher adhesivity, a larger specific surface area and a greater strength has been required.

[0004] For satisfying these demands, a great number of attempts have been made to apply the phase separation phenomenon of blend polymers to a method for producing a super-fine synthetic fiber. For example, Japanese Patent Publication 10617/1974, Japanese Patent Publication 17609/1976 and Japanese Patent Application Kokai (Laid-open) 56925/1973 describe individually that a fibril can be generated by beating a sea-islands fiber comprising PAN as the sea component and PVA graft-copolymerized with acrylonitrile or a poly (methyl methacrylate) polymer as the islands component.

[0005] According to the techniques described in these publications, however, a mixture of water and the solvent of a stock solution or a single organic solvent having the solidifying potency is used in a solidifying bath because PAN is the sea component. However, not any uniform gel yarn can be recovered from such techniques because of the strong solidifying action, involving difficulty in higher drawing. Hence, it is difficult to produce a fiber with excellent reinforcing performance and a higher strength, in a stable and inexpensive manner industrially.

[0006] Because the compatibility of the polymers is so enhanced with the addition of a graft polymer that the spinning solution turns transparent to hardly form a phase separation structure, not only fibrillation then gets hard but also the resulting fibril is too thin and so readily tangled, involving a problem in that a fiber ball may readily be formed.

[0007] Furthermore, Japanese Patent Publication 31376/1972 discloses a readily fibrillatable PVA fiber comprising a completely saponified PVA as the sea component and a partially saponified PVA as the islands component, but the fiber has drawbacks such that the partially saponified PVA is solubilized during the beating process in water so that a specific system or a specific chemical reagent will be needed so as to treat the water used for the beating; that an increased volume of foam may be generated during the beating, which disturbs the beating process; and that the beatability of the fiber is not essentially satisfactory because the sea component and the islands component both comprise PVA polymers.

[0008] Therefore, a fiber principally comprising PVA, having a higher strength, being readily fibrillatable and highly dispersible and having a sufficient reinforcing effect, has been demanded. But such fiber has not been generated yet. Thus, it is the object of the present invention to provide readily fibrillatable fiber satisfying the desirable performance described above.

[0009] This object has been achieved by a readily fibrillatable fiber of a sea-islands cross section, comprising PVA (A) and a vinyl polymer (B) substantially free of vinyl alcohol units, wherein the components (A) and (B) serve as the sea component and the islands component, respectively, characterized in that the fiber has a strength of 6 g/d or more and a beatability of 30 minutes or less. Such readily fibrillatable fiber can be produced by dissolving PVA (A) and the polymer (B) in an organic solvent to prepare a spinning solution, wet spinning or dry jet wet spinning the resulting spinning solution into a solidifying bath of a mixture of a solidifying solvent and water so as to form a specific system or a specific chemical reagent.
organic solvent of the spinning solution from the fiber in an extraction bath, and drawing the resulting yarn, provided that the following conditions 1 to 3 should be met:

1. the spinning solution is of a phase separation structure in which particles of a particle size of 2 to 50 µm, comprising the solution of the polymer (B), are present in the solution of the polymer (A);
2. the solidifying solvent is an organic solvent and the solidifying bath includes the organic solvent of the spinning solution at 15 to 75 % by weight; and
3. the total draw ratio is 8 or more.

[0010] Figs. 1 and 2 depict examples illustrative of the cross section of the fiber of the present invention, wherein the dotted island parts (parts marked with a numerical figure "1" in the figure) are composed of the polymer (B) while the slashed sea part (part marked with a numerical figure "2" in the figure) is composed of PVA (A), and blank parts present in the boundaries between the PVA (A) and the polymer (B) (parts marked with a numerical figure "3") are void parts.

[0011] The fiber of the present invention is a fiber of a sea-islands cross section, substantially comprising PVA (A) and a vinyl polymer (B) substantially free of vinyl alcohol units, wherein the component (A) is the sea component and the component (B) is the islands component. Particularly when a PAN polymer is used as the polymer (B), a fiber with a particularly high strength can be produced because PVA and PAN both have highly polar groups. The fiber is excellent as a reinforcing material because the fiber has a higher adhesivity to cement, rubber and the like and a higher thermal resistance: additionally, the fiber has so high hydrophilicity that the fiber is preferable for use in wiper materials of which wiping performance is significant.

[0012] In accordance with the present invention, the term "PVA (A)" means a polymer containing the vinyl alcohol unit at 70 mole % or more, and the polymer may therefore be copolymerized with monomers at a ratio of less than 30 mole %, satisfactorily, such as ethylene, vinyl acetate, itaconic acid, vinyl amine, acrylamide, vinyl pivalate, maleic anhydride, and a vinyl compound containing sulfonic acid. Preferably, such polymer has a saponification degree of 80 mole % or more, and for orientation and crystallization. preferably, the polymer contains the vinyl alcohol unit at 95 mole % or more, more preferably 98 mole % or more, and still more preferably 99 mole % or more and most preferably 99.8 mole % or more. The polymerization degree of PVA is not with specific limitation, but is preferably 500 or more, more preferably 1500 or more. so as to produce a fibril of a higher strength. So as to improve the hot-water resistance. PVA may be acetalated and cross linked within the molecule or between the molecules with formaldehyde, glutaraldehyde and the like, at a post-reaction after such fiber preparation. Additionally, PVA may be cross linked with other cross-linking agents, besides those described above.

[0013] In accordance with the present invention, use is made of a vinyl polymer (B) substantially free of vinyl alcohol units as the islands component, because the vinyl polymer readily forms a spinning solution of a good phase separation structure when mixed with the PVA (A) in a solvent. Furthermore, the polymer (B) is preferably a vinyl polymer with no water swelling because such polymer is readily fibrillated in combination with PVA (A). The term "polymer with no water swelling means a polymer with a water absorption ratio below 20 % by weight, when a 100µm-thick non-porous film prepared from the polymer is immersed in water at 20 °C to absorb water up to its saturation state. In accordance with the present invention. PAN is illustrated as the most preferable example of the polymer (B) as described above; and another preferable example includes a methyl methacrylate polymer (abbreviated as "PMMA" hereinafter).

[0014] The PAN in accordance with the present invention should satisfactorily contain the acrylonitrile unit at 70 mole % or more, and thus, the PAN may be copolymerized with monomers at a ratio of less than 30 mole %. satisfactorily, such as (meth)acrylic esters for example methyl acrylate, ethyl acrylate, and methyl methacrylate; vinyl esters for example vinyl acetate and vinyl lactate; vinyl compounds for example vinyl chloride; unsaturated carboxylic acids for example acrylic acid, methacrylic acid, and maleic anhydride; and vinyl compounds containing sulfonic acid. So as to improve the solubility in the solvent of the spinning solution, preference is given to a PAN copolymer with other vinyl monomers copolymerized therein at a ratio of 0.5 to 10 mole %, more preferably 2 to 8 mole %, rather than PAN homopolymer.

[0015] Furthermore, the PMMA should satisfactorily contain the methyl methacrylate unit at 80 mole % or more, and therefore, the PMMA may be copolymerized with for example methyl acrylate and ethyl acrylate within a range up to 20 mole %. Preferably, in particular, the PMMA to be used in accordance with the present invention is copolymerized with methacrylic ester at 2 to 20 mole %, because such PMMA may readily form a solution of the sea-islands phase separation structure as described below; and from the same reason, the PMMA is preferably at a polymerization degree of 300 to 2,000.

[0016] In accordance with the present invention as has been described insofar, PVA should be the sea component while the polymer (B) should be the islands component, and the weight ratio of A/B therefor should be 80/20 to 42/58. When PVA (A) is below 42 % by weight, the PVA (A) and the polymer (B) both may so highly solubilized into the solidifying bath that inter-fiber fusion is readily induced and not any well-defined phase separation state with the PVA (A) as the sea component can be prepared. When PVA (A) is above 80 % by weight, the number of the islands component may become small and therefore the fibrillation may become difficult.
From the respect of strength, the fibrillation of a recovered fiber and the dispersibility of a yielded fibril, in particular, the (A)/(B) ratio in weight should preferably be 70/30 to 50/50.

[0017] The fiber of the present invention should have a strength of 6 g/d or more. The term "strength" in accordance with the present invention means the tensile strength measured according to JIS-L 1015. If the strength is less than 6 g/d, then, the reinforcing performance for cement, rubbers and resins is insufficient. In accordance with the present invention, the strength should be preferably 7 g/d or more, and particularly preferably 8 g/d or more.

[0018] The beatability of the fiber of the present invention should be 30 minutes or less. The term "beatability" in accordance with the present invention refers to the duration of agitation and beating as measured as follows; leaving to stand a fiber sample (4 g) in atmosphere at 20 °C and a relative humidity of 65 %, cutting the sample into 2-mm pieces, adding water (400 cc) at 20 °C into the cut sample and charging the sample in a mixer manufactured by Matsushita Electric Industry Co. Ltd. (National MX-X40) prior to agitation and beating at 11,000 rpm for a given period of time, subsequently sampling the beaten solution in water dispersion and measuring the filtered water time by the method described below, the duration of agitation and beating required for the filtered water time to reach 60 seconds is referred to as beatability. The term "filtered water time" in accordance with the present invention means a time required for filtering a water dispersion (750 cc) containing a fibril of 0.5 g through the aforementioned measuring cylinder with a metal filter mounted on the open-bottom part, after 5-minute beating under the same conditions as those for measuring the beatability as described above.

[0019] The beatability above 30 minutes is so insufficient that the fiber is never fibrillated sometimes when used practically. A longer duration of beating may lead to poor dispersibility of the resulting fibril, which consequently tends to form fiber balls. It is needless to say that even a fiber with poor fibrillatability may possibly be fibrillated by methods such as the prolongation of the duration of beating or the application of more severe beating conditions, but the fibril produced in such manner is at a state such that fibrils have tangled to each other or fibrils have been cut further in shorter pieces, so such fibril is not suitable for the intended use. The reason why such longer duration of beating generally deteriorates the fibril dispersibility is not evident, but it is possibly due to the fact that such fibril is so thin to be readily tangled. The presence or absence of the formation of fiber balls is determined as follows. Placing a beating solution (40 cc) in a 300-cc beaker, subsequently adding a viscous agent (aqueous 0.1 polyethylene oxide solution) and water to the solution to a final solution volume of 200 cc, and sufficiently agitating the resulting solution by means of a glass bar, fibrils tangling to each other or fibrils tangling to the fibers, in this dispersion, may form fiber balls of a diameter of 3 mm or more, which cannot be disintegrated with an agitation procedure alone with a glass bar. The presence or absence of the fiber balls should be determined under observation.

Characteristically, the fiber of the present invention hardly forms fiber balls. The reason is not essentially evident, but may potentially reside in the use of an organic solvent in the solidifying bath.

[0020] The fiber of the present invention preferably has a filtered water time of 75 seconds or more after 5 minute beating. Such fiber can be produced by the processes described below. The term "filtered water time after 5-minute beating" (simply referred to sometimes as "filtered water time" hereinbelow) means a time required for passing a water dispersion (750 cc) containing a fibril of 0.5 g through the aforementioned measuring cylinder with a metal filter mounted on the open-bottom part, after 5-minute beating under the same conditions as those for measuring the beatability as described above.

[0021] In the cross section of the fiber of the present invention, furthermore, voids are present on the periphery of a part or most part of the island components of a diameter larger than 0.2 μm. As described above, Fig. 1 depicts one example of the cross section of the fiber in accordance with the present invention on the basis of the microscopic pictures, wherein dotted island parts correspond to the polymer (B), while the slashed sea part corresponds to the PVA (A), and the blank parts present in the boundaries between the PVA (A) and the polymer (B) correspond to the void parts described above. Via the presence of such void parts in the fiber of the present invention, the beatability of the fiber is enhanced far greatly. If the polymer (B) is PAN, in particular, the number of islands with a void increases. When a spinning solution does not have a phase separation structure, such void does not develop. The void may possibly be generated during the extraction of the solvent from the spinning solution for wet spinning or dry-jet wet spinning and during the dry process, but such void substantially is not generated at processes for melt spinning or dry-type spinning.

[0022] Based on the microscopic pictures, Fig. 2 depicts one example of the cross section of a fiber with a filtered water time of 75 seconds or more, produced by a method described below. The area of void parts present in between the islands and the sea. In Fig. 2, is larger than the area in Fig. 1. A part of islands of an average diameter larger than 0.4 μm has voids in common to adjacent islands. These larger common voids more readily induce further fibrillation. The term "average diameter" of an island means the diameter of a circle corresponding to the cross sectional area of the island.

[0023] Description will now be made of a method for producing the fiber of the present invention. Firstly, PVA (A) and the polymer (B) are dissolved in an organic solvent to prepare a spinning solution. Such organic solvent includes polar organic solvents, for example, dimethyl sulfoxide (DMSO), dimethylacetamide and dimethyl...
ylformamide. From the respect of properties of low-temperature dissolution, low decomposition of the polymers, and ready fibrillation, preference is given to DMF. The total polymer concentration of the PVA (A) and the polymer (B) in the spinning solution is preferably within a range of 10 to 30 % by weight. Furthermore, the temperature of the spinning solution is preferably within a range of 50 to 120 °C.

[0024] The spinning solution produced by the method of the present invention should be of a phase separation structure at particle sizes of 2 to 50 μm. The term "phase separation structure" of the spinning stock solution in accordance with the present invention refers to a state with observed particles, when the spinning solution is dropwise added onto a slide glass to a final thickness of about 200 μm to photograph the solution by a differential interference microscope Type BX-60 manufactured by Olympus Optical Co. Ltd. From the respect of strength and high modulus and additionally from the respect of ready fibrillation in accordance with the present invention, PVA (A) and the polymer (B) should be present in a phase separation state wherein the polymer (B) is the dispersed component (islands component) and the component PVA (A) is the component functioning as the dispersing medium. The term "particle sizes of 2 to 50 μm" in accordance with the present invention means that most of particles identified by the differential interference microscope have diameters within the range. Most of particle sizes, if above 50 μm, are not preferable in terms of the stability of the stock solution and the spinning stability; most of particle sizes, if below 2 μm, are neither preferable because the phase separation is so insufficient that the beatability of the resulting fiber is deteriorated. A phase separation structure at particle sizes of 3 to 45 μm is more preferable. Because the particles in the spinning solution serve as nuclei during solidification, the particle size is significant for forming a readily fibrillatable fiber.

[0025] The particle size in the spinning solution may be measured by the following method, in addition to the method described above. More specifically, coating the spinning solution onto a slide glass to a final thickness of about 100 μm and solidifying the solution with methanol at room temperature to prepare a film which is to be observed with an optical microscope of 500 magnifications, the diameter of a particle then identified should be measured and defined as the particle size (the method is referred to as "particle size by the methanol solidification method" hereinafter). In accordance with the present invention, most of particles identified by the method of methanol solidification have diameters within a range of 1 to 20 μm, which range corresponds to the sizes of 2 to 50 μm, identified by the differential interference microscope. Further, the term "particle size" simply referred to in accordance with the present invention means a value measured by means of the differential interference microscope.

[0026] The factors determining the phase structure of the spinning solution include the compatibility of the two polymers, namely PVA (A) and the polymer (B), the composition ratio of the two polymers, the conditions for agitating the spinning solution, and the like. With respect to the compatibility of the two polymers, poorer compatibility thereof (meaning a lower compatibility) involves a larger particle size; with respect to the composition ratio, meanwhile, a polymer at a larger ratio serves generally as the sea component. In addition to these factors, a significant factor determining the particle size is the agitation conditions during the dissolution. Generally, preference is given to the agitation conditions to a peripheral speed of 1 to 10 m/sec, although the conditions may vary more or less, depending on the type of an agitator or the shape of an agitation wing. Above 10 m/sec, the particle size may get too small; less than 1 m/sec, alternatively, the dissolution or dispersed state of the polymers may be insufficient.

[0027] The peripheral speed of 2 to 5 m/sec is particularly preferable. The particle state is essentially determined by a combination of the polymers, and so as to prepare a desirable particle size from the combination, the composition ratio of the two polymers, the polymer concentrations, the additives in the spinning solution, the dissolution rates and agitation rate should be adjusted appropriately. For simplification, in particular, the peripheral agitation speed should be selected within a range of 1 to 10 m/sec, to prepare a spinning solution of which particle size is then measured. Based on the results, the agitation conditions should be modified to adjust the particle size.

[0028] By adjusting the particle size within a range of 2 to 50 μm in such manner and selecting the conditions for a solidifying bath and those for drawing as described below, the processability such as spinnability and drawing performance can be established in combination with the properties such as ready fibrillatability and strength. The viscosity of the spinning solution is preferably within a range of 10 to 400 poises for wet spinning or within a range of 50 to 2,000 poises for dry-jet wet spinning.

[0029] The spinning solution thus produced is then passed through a spinning nozzle for wet spinning or dry-jet wet spinning in a solidifying bath. Because the wet spinning process comprises directly contacting the solidifying bath with the spinning nozzle it is possible to spin without fibrous fusion even if the pitch of the nozzle orifices is narrowed. Thus the process is suitable for spinning by means of a multi-orifice nozzle. Alternatively, a dry-jet wet spinning where an air gap is arranged between the solidifying bath and the spinning nozzle is suitable for high-speed spinning because of a larger drawing at the air gap part. In accordance with the present invention, the wet-type process or dry-jet wet process may be appropriately selected, depending on the object and use.

[0030] In accordance with the present invention, an organic solvent is used as the solidifying solvent in the solidifying bath, along with a mixture solution of the so-
The spinning solution contained in the yarn. Furthermore, in the solidifying bath into an extraction bath to remove to dry heat drawing process. For leading the yarn formed an oiling agent, drying and the like, prior to the transfer of the solvent of the spinning solution, addition of the solidifying solvent and the solvent of the spinning solution, which gives preferable influences over the performance of the readily fibrillatable fiber.

**[0031]** So as to maintain an appropriate solidification level by the method in accordance with the present invention, the composition ratio of a solidifying organic solvent in the solidifying bath and the solvent of the spinning solution is of importance; in accordance with the present invention, a range of 25/75 to 85/15 in weight ratio is selected. If the level of the solvent of the spinning solution in the solidifying bath is less than 15 %, the solidifying potency is too high, which causes break at the nozzle and poor spinning tone. Additionally, the fiber performance represented by the strength of the resulting fiber is likely to be deteriorated. If the concentration of the solvent of the spinning solution in the solidifying bath is more than 75 %, no satisfactory solidification can be induced, involving the deterioration of the spinning processability. Thus, not any fiber with satisfactory performance from the respect of strength can be produced. More preferably, the concentration of the solvent in the spinning solution in the solidifying bath was within a range of 20 to 70 % by weight; most preferably, the level is within a range of 30 to 65 % by weight. As has been described above in accordance with the present invention, a mixture solution of an organic solidifying solvent and the solvent of the spinning solution is used in the solidifying bath, but it is needless to say that smaller amounts of liquids or solids, besides them, may be dissolved and present in the solidifying bath. In accordance with the present invention, the most preferable combination of the solidifying solvent and the solvent of the spinning solution is a combination of methanol and DM-MSO.

**[0032]** The gel yarn passing through the solidifying bath is transferred to processes of wet drawing, extraction of the solvent of the spinning solution, addition of an oiling agent, drying and the like, prior to the transfer to dry heat drawing process. For leading the yarn formed in the solidifying bath into an extraction bath to remove the spinning solution contained in the yarn. Furthermore, use of a final extraction bath comprising three components of alcohols, ketones and water with a weight ratio of the alcohols and ketones at 9/1 to 1/9 and a water content at 1 to 30 % by weight of the total weight of the three components, can yield a very excellent, readily fibrillatable fiber, satisfying the required performance of a filtered water time of 7 seconds or more. The alcohols in the final extraction bath include for example methanol, ethanol, propanol and butanol. Also, such ketones include for example methyl isopropyl ketone, methyl-n-buty1 ketone, and methyl isobutyl ketone; ketones having a higher boiling point than that of water, for example methyl-n-buty1 ketone and methyl isobutyl ketone, are preferable from the respect of generating more excellent, ready fibrillatability. If the weight ratio of the alcohols and the ketones is outside the range of 9/1 to 1/9, the resulting beatability may not be very excellent. If the water content is less than 1 % by weight, the beatability is neither very excellent; if above 30 % by weight, the fibers fuse to each other, causing the deterioration of the strength and the like of the fibers. By using such final extraction bath composed of the specific three components, a fiber satisfying the condition such that the filtered water time should be 75 seconds or more as described above can be produced, and the cross section of the resulting fiber is such that a part of islands of an average diameter larger than 0.4 μm has voids in common to adjacent islands, as shown in Fig. 2.

**[0033]** The thus produced spun yarn is dried and subsequently drawn by dry heating. The dry heat drawing process is significant for the method of the present invention; more specifically, the dry heat drawing should be done to a final total draw ratio of 8 or more. The term "total draw ratio" means a magnification represented by a wet draw ratio multiplied by a dry heat draw ratio, and when the total draw ratio is less than 8, neither a fiber with a greater strength nor a readily fibrillatable fiber can be generated.

**[0034]** The factors to make the total draw ratio above 8 include the PVA (A)/polymer (B) composition ratio, the conditions of the solidifying bath such as the composition and temperature of the solidifying bath, and wet drawing conditions such as wet draw ratio, dry heat drawing conditions such as dry heat drawing temperature and residence time (drawing rate) in dry heat drawing atmosphere. With respect to the composition ratio of PVA(A)/polymer (B), a higher PVA(A) volume ratio can enhance the total draw ratio; an increased ratio of the solvent of the spinning solution in the solidifying bath can lower the total draw ratio; or a higher temperature of the solidifying bath can increase the total draw ratio. In accordance with the present invention, furthermore, the temperature of the solidifying bath is preferably within a range of -5 to 20 °C. Additionally, a larger wet draw ratio tends to induce the increase of the total draw ratio; a higher dry heat drawing temperature increases the total draw ratio; or a longer residence time in drawing atmosphere furthermore elevates the total draw ratio. In
accordance with the method of the present invention, still furthermore, the wet draw ratio, the dry heat drawing temperature and the residence time should preferably be within ranges of 1.5- to 4.5-fold, 210 to 250 °C and 5 to 90 seconds, respectively. So as to generate the total draw ratio at a desirable value, thus, spinning and drawing firstly be conducted under appropriate conditions; and then, at least one of the factors should be modified on the basis of the resulting total draw ratio, to readily change the total draw ratio to the desirable value.

For the method of the present invention, the total draw ratio should be preferably 10 or more, more preferably 12 or more. The fiber after dry heat drawing may satisfactorily be treated with dry heating, shrinkage process, and further, with formal process so as to improve the hot-water resistance, and acetal process via dialdehyde and the like, and cross-linking process via long-chain alkyl phosphate and the like.

Within the scope of the objects of the present invention, still additionally, the fiber of the present invention may or may not contain an inorganic pigment, an organic pigment, a thermal deterioration preventive agent, a pH adjusting agent, a cross-linking agent, an oiling agent, a variety of stabilizers and the like, in addition to the PVA(A) and the polymer (B), which may be added at individual production stages, such as the stage of the spinning solution, the solidifying stage, the extraction stage, immediately before drying, before heat drawing, after heat drawing and after post-reaction.

As has been described above, the fiber thus produced contains such islands with voids in the boundaries between PVA (A) and the polymer (B) that a fibril of a size of about 1 μm can be readily produced through the single application of chemical expanding force or mechanical stress or the combined application thereof. Fibrillation methods representatively include a method comprising fibrillating a fiber and forming the resulting fibril into a sheet form; a method comprising forming a fiber into a sheet form prior to fibrillation; and a method comprising mixing a fiber into rubber, cement and plastics and fibrillating the fiber during kneading.

Herein, a first method comprises cutting the fiber of the present invention into short pieces of 1 to 30 mm, immersing and dispersing the pieces into water, fibrillating the pieces through mechanical stress by means of beater, refiner, mixer and the like, and making paper from the resulting fibril as a paper material. The sheet produced by the method is in the form of a fine fiber due to fibrillation, so that a thin and strong paper of a higher tension can be produced. When a fibril is mixed with inorganic micro-particles or micro-particles of a thermo-setting resin under agitation, such particles can be captured into the fibril to be then fabricated, thus generating a friction material suitable for brake shoe and clutch plate.

A second method comprises crimping and cutting the fiber of the present invention into a staple, subsequently passing the staple through a carding machine to form a web, and applying a high-pressure water jet of 30 kg/cm² or more, preferably 60 kg/cm² or more onto the web, thereby fibrillating the fiber of the present invention via the impact or shear of the high-pressure water jet; or the method may comprise cutting the fiber of the present invention into pieces of 1 to 30 mm, dispersing the pieces as a paper material in water to prepare a base paper by wet process, and applying a high-pressure water jet of 30 kg/cm² or more, preferably 60 kg/cm² or more onto the paper, thereby fibrillating the fiber of the present invention via the impact or shear of the high-pressure water jet. Because of the fibrillation with a high-pressure water jet after web formation, the method is advantageous in that poor dispersion or high density of the fibrils can be avoided to produce a porous, soft, two-dimensional sheet although the sheet comprises a super-fine fiber. The sheet is useful as wiper and filter.

Furthermore, a third method comprises fibrillating a fiber by applying shear force to the fiber added during rubber mastication, the agitation of cement slurry or the melt kneading of plastics, and therefore, the method is superior in that no specific process is needed to fibrillate the fiber. Hence, the method is suitable for producing fiber-reinforced rubber products, fiber-reinforced cement products and fiber-reinforced plastics products.

Fibrillation of fibers via high-pressure water jet has been carried out conventionally, but the processability prior to such high-pressure water jet process and fibrillation have not been compatible to each other because they are in reverse correlation. More specifically, a fiber readily fibrillatable at a high pressure water jet process is so readily fibrillated at processes of spinning, drawing, crimping and carding, to cause a trouble in the processing. Adversely, a staple with lower fibrillation, with no trouble in the processability prior to the web formation process, is hardly fibrillated at high-pressure water jet process, so that a nonwoven fabric comprising a super-fine fiber tends to be hardly produced. As has been described above, however, the fiber of the present invention has lower fibrillation at its dry state prior to the high-pressure water jet process. Therefore, the trouble due to fibrillation may be less at the dry process; and at its wet state with high-pressure water jet, the inner deformation is enlarged so instantly through the expansion of PVA (A) constructing the fiber, that fibrillation is readily induced in the fiber via high-pressure water jet.

Because the fiber of the present invention is also fibrillatable through a strong, mechanical shear force alone, a needle punch method is additionally used as one of the fibrillation methods. As has been described above, herein, the fiber of the present invention is far more fibrillated with a mechanical shear force at its state with wet deformation, as is the case of water-jet process. Thus, the needle punch method without wet deformation should be conditioned strictly. In other words, the fibrillation should be carried out under the conditions of a punching density of preferably 250 needles/cm² or
more, and more preferably 400 needles/cm² or more.

[0043] For both the water-jet method and the needle punch method, generally known any process may be satisfactory, for example, carding processes such as roller card, semi-random card, and random card, and web formation processes such as tandem web, cross web, and crisscross web.

[0044] Papers produced by generally known paper making machines of cylinderer paper machine, fourdriner paper machine and the like, may be satisfactory as the paper to be used by the wet water-jet method: any paper at a dry state or at a state prior to drying may be satisfactory, if the paper can be introduced into a water-jet process.

[0045] As the raw material to be mixed into a web or into a paper, together with the fiber of the present invention, use is made of generally known materials including natural pulp, synthetic pulp, cotton, linen, rayon, solvent-spun cellulose fiber, polymeric rayon, acetate fiber, polyester fiber, acrylic fiber, nylon fiber, polypropylene fiber, vinylon and the like. As to the web lamination, webs of different mixing ratios of the fiber of the present invention may satisfactorily be laminated together or a web of the fiber of the present invention may satisfactorily be laminated to a web with no containment of the fiber of the present invention. In other words, the fiber of the present invention may partially be contained in a web at its fibrillated state, satisfactorily. Therefore, the fiber may be present not uniformly but unevenly, satisfactorily. To the resulting dry-type nonwoven fabric, wet-type nonwoven fabric, or needle punch dry-type nonwoven fabric may be added generally known resin binders such as vinyl acetate-, acrylic-, polyethylene-, vinyl chloride-, urethane-, polyester-, epoxy-, rubber binders by the emulsion binder imparting method and powder imparting method, including saturation method, spraying method, printing method, and foaming method.

[0046] The present invention will now be described more specifically in examples, but the present invention is not limited to these examples.

Example 1

[0047] PVA of a polymerization degree of 1,750 and a saponification degree of 99.8 mole % and PAN (of a water absorption ratio of 5 % or less) copolymerized with methyl methacrylate at 5 mole % were dissolved in DMSO under agitation at a peripheral speed of 3 m/sec at 100 °C in nitrogen stream by means of an agitator having an inclined puddle wing for 8 hours, to produce a mixture spinning solution of a weight ratio of PVA/PAN of 50/50 and a polymer concentration of 20 % by weight. The spinning solution was opaque under visual observation; under the observation of the phase structure by the differential interference microscope described above, the structure was mostly in phase separation at particle sizes of 2 to 50 μm, while the particle sizes measured by the methanol solidification method were within a range of 3 to 10 μm. Coating the spinning solution on a glass plate to a final thickness of about 200 μm and immersing the plate as it was in methanol at room temperature, followed by hot water process, it was confirmed that the PVA component was the component of the dispersing medium (sea component) while the PAN component was the dispersed component (island component). The spinning solution was left to stand for de-foaming for 8 hours, but it was verified that no tendency was observed that the dispersed particles would aggregate to grow into a larger particle and that the solution had an absolutely stable phase structure.

[0048] Passing the spinning stock solution at 80 °C through a spinning nozzle of 1,000 orifices of a diameter of 0.08 mm to wet spin the solution in a solidifying bath of a DMSO/methanol weight ratio of 50/50 and a temperature of 10 °C subjecting to wet drawing of 3-fold, extracting the DMSO contained in the yarn into methanol, drying the resulting yarn in hot air at 80 °C, prior to dry heat drawing at 230 °C to a total draw ratio of 18 (the residence time in the dry heat drawing bath was 30 seconds), a PVA/PAN blend fiber of a total 1,800 denier and 1,000 filaments was produced. The microscopic examination of the cross section of the fiber indicates that the PVA corresponded to the sea while the PAN corresponded to the islands and that voids were present in at least part of the boundaries between a part of the island components of a diameter larger than 0.2 μm and the sea component. The fiber had a strength of 8.5 g/d and a Young's modulus of 180 g/d. The fiber was then cut into pieces of a length of 2 mm, which were dispersed in water, followed by beating by means of the mixer for 5 minutes, The resulting beaten solution was observed with an optical microscope. Most of the fibers were fibrillated into a fibril of a size of about 1 μm. Further, the filtered water time of the beaten solution after the 5-min beating was measured to be 70 seconds. The fiber beatability defined by the present invention was within 5 minutes. The dispersibility of the beaten solution was excellent, with no observed fiber ball derived from the tangle of fibrils to each other. By cutting the fiber of the present Example into pieces of a length of 3 mm, and beating the pieces by means of a refiner followed by paper making, a paper of a higher er density and a higher strength was produced.

[0049] Crimping the fiber produced in the Example and cutting the resulting fiber into 51-mm pieces to produce a staple, carding the staple yields a card web, which was then subjected to a high-pressure water jet process at 80 kg/cm². Scanning electron microscopic observation of the surface of the resulting nonwoven fiber indicated that most of the fibers were fibrillated into a fibril of a size of about 1 μm. Using the nonwoven fabric to wipe the stain of a pair of glasses, the stain was very cleanly wiped off. No problem developed even after washing the nonwoven fabric in water, so the fabric could be used as a wiper in a repeated fashion.

[0050] Furthermore, the PVA/PAN blend fiber was
added to natural rubber followed by kneading. Through the shear force during the kneading, the fiber was fibrillated in the form of dispersion in the rubber. The rubber composition was molded into a sheet of a thickness of 2 mm, which was shown to be an extremely strong sheet in the fibril length direction.

Comparative Examples 1 and 2

[0051] Fibers were produced under almost the same conditions as in Example 1, except that the weight ratios of PVA/PAN were 9/1 (in Comparative Example 1) and 1/9 (Comparative Example 2). In Comparative Example 1, the DMSO concentration in the solidifying bath was decreased from 50 % to 30 %, whereby smooth spinning was achieved, with drawing at a total draw ratio of 15. The resulting fiber of Comparative Example 1 had a strength of 12.5 g/d and a Young’s modulus of 230 g/d. However, the fiber was so poorly beatable that the fiber was hardly fibrillated after agitation and beating for 60 minutes. Comparative Example 2 showed poor spinnability and poor drawability, with no normal fiber produced.

Comparative Example 3

[0052] A fiber was produced under almost the same conditions as in Example 1, except that the dry heat draw ratio was modified to a final total draw ratio of 6, provided that the discharge flow was adjusted so that the single yarn fineness might be the same as in Example 1. The resulting fiber had a lower strength of 4.1 g/d and a lower Young’s modulus of 89 g/d than those of Example 1. Compared with the beatability of Example 1, the beatability of the fiber was poor, but it was substantially as good as 15 to 20 minutes. From the respect of rubber reinforcement, however, the fiber had far poorer than that of Example 1, which was demonstrated as the lower Young’s modulus of the fiber-reinforced rubber.

Example 2

[0053] A spinning solution was prepared in the same manner as in Example 1, except that the PVA/PAN weight ratio was modified to 60/40 and the peripheral speed of an agitator was 5 m/sec. The spinning solution was opaque under visual observation; under observation of the phase structure by the method described above, a phase separation structure containing particles most of which had particle sizes within a range of 2 to 50 μm was formed; and the particle sizes measured by the methanol solidification method were within a range of 2 to 8 μm. It was verified by the same hot water process after film preparation as in Example 1, that PVA was the dispersing medium component (sea component) and the PAN component was the dispersed component (islands component) in the spinning solution. The spinning solution was left to stand for 8 hours for defoaming, but no tendency was observed such that dispersed particles would aggregate to form a larger particle. It was thus confirmed that the spinning solution formed an absolutely stable phase structure. The spinning solution of 80 °C was wet spun into the solidifying bath of a DMSO/methanol of 45/55 at a temperature of 5 °C, through a spinning nozzle of 1,000 orifices of a diameter of 0.08 mm, wet drawn of 3-folds, followed by extraction of the DMSO contained in the yarn into methanol and drying in hot air at 80 °C. Subsequently, the resulting yarn was subjected to dry heat drawing at 230 °C to a final total draw ratio of 16 (the residence time in the drawing bath was 30 seconds), to produce a PVA/PAN blend fiber of 1,800 d/1,000 f.

[0054] As shown in Fig. 1, the observation of the cross section of the fiber demonstrated that PVA corresponded to the sea while PAN corresponded to islands, and most of islands of a diameter larger than 0.2 μm had voids in at least part of the boundaries with the sea component. The fiber had a strength of 9.5 g/d and a Young’s modulus of 210 g/d. The beatability of the fiber was 10 minutes while the filtered water time after 5-min beating was 20 seconds, never involving the formation of any fiber ball. Adding the fiber to rubber as in Example 1 for mastication and molding the resulting mixture into sheet, a sheet of a very high strength was yielded as in Example 1.

Comparative Examples 4 and 5

[0055] The DMSO concentration in the solidifying bath in Example 1 was modified to 10 % by weight (Comparative Example 4), with the resultant frequent yarn break at the nozzle part. The resulting fiber had a beatability above 30 minutes, while the filtered water time after 5-min beating was 4 seconds or less. Thus, it was difficult to fibrillate the fiber. The DMSO concentration modified to 80 % by weight (Comparative Example 5) caused the deterioration of the solidification and spinnability, so no normal spun base yarn could be produced.

Comparative Example 6

[0056] In the same manner as in Example 2, PVA-grafted PAN (radically polymerized acrylonitrile in the presence of PVA, having a grafting ratio of 75 %) was mixed with PVA at a grafted PAN/PVA weight ratio of 40/60 prior to dissolution. The spinning solution thus produced was transparent and homogeneous with no sea-islands phase structure observed with a differential interference microscope. In the same manner as in Example 2, the spinning solution was spun and drawn. The spinning and drawing tones were smooth. The resulting fiber of a strength of 9 g/d and a Young’s modulus of 200 g/d was as good as the fiber of Example 2, but the fiber was hardly beatable, as shown in the beatability of 50
minutes or more and the filtered water time after 5-min beating of 4 seconds or less. The PVA-grafted PAN showed good compatibility with PVA, never forming a phase separation structure at the stage of the spinning solution. Because the PAN was present in a uniform and fine dispersion at a state close to molecular dispersion in the fiber, it was concluded that the fiber was thus hardly fibrillatable.

Example 3

[0057] The dissolution and spinning of the spinning solution was conducted as in Example 1, except that use was made of poly(methyl methacrylate) having been copolymerized with methyl acrylate at a ratio of 10 mole % and having a polymerization degree of 1,000 (Parapet G-1,000; manufactured by KURARAY CO., LTD.; abbreviated as “PMMA”, hereinafter) in place of PAN and that the weight ratio of PVA/PMMA was 60:40. The resulting spinning solution was opaque; and under observation with a differential interference microscope, the solution was of a phase separation structure wherein most of the particles were within a particle size range of 2 to 50 μm, while the particle sizes measured by the methanol solidification method were within a range of 2 to 10 μm. The observation of the resulting spinning solution in the same way as in Example 1 demonstrated that the solution was of a sea-islands structure wherein PVA was the sea component.

[0058] Furthermore, the observation of the cross section of the resulting fiber indicated that PVA corresponded to the sea while PMMA corresponded to the islands; that distinct but narrower voids than those in Examples 1 and 2 were present in a part of the boundaries with the sea component on the periphery of a part of islands of a diameter larger than 0.2 μm in between the sea component and the island components; and the fiber had a strength of 8.7 g/d and a Young's modulus of 190 g/d. The beatability of the resulting fiber was 10 minutes, while the filtered water time after 5-min beating was 15 seconds. No fiber ball formation was observed.

Example 4

[0059] PVA of a polymerization degree of 1,750 and a saponification degree of 99.8 mole % and PAN (a water absorption ratio of 10 % or less) copolymerized with vinyl acetate at a ratio of 5 mole % were dissolved in DMSO under agitation at a peripheral speed of 3 m/sec at 100 °C in nitrogen stream by means of an agitator with an inclined puddle wing for 10 hours, to produce a spinning solution of a weight ratio of PVA/PAN of 50/50 and a polymer concentration of 20 % by weight. The spinning solution was opaque under visual observation; the particle size was measured by the differential interference microscope, with the results that most of the particles were within a range of 2 to 50 μm; the particle sizes measured by the methanol solidification method were within a range of 3 to 10 μm. It was confirmed at a hot-water process that the PVA component was the component of the dispersing medium (sea component) while the PAN component was the component dispersed (islands component). The spinning solution was left to stand for defoaming for 8 hours but it was verified that no tendency was observed that the dispersed particles would aggregate to grow into a larger particle and that the solution had an extremely stable phase structure.

[0060] Passing the spinning solution at 100 °C through a spinning nozzle of 1,000 orifices of a diameter of 0.08 mm to wet spin the solution in a solidifying bath of a DMSO/methanol weight ratio of 30/70 and at a temperature of 5 °C, subjecting to wet drawing of 3-fold, extracting the DMSO contained in the yarn into methanol, passing the yarn through a final extraction bath composed of three components, namely methanol/methyl isobutyl ketone (abbreviated as “MIBK”)/water = 55.8/38.2/6, adding an oiling agent to the resulting yarn, and drying the yarn in hot air at 80 °C yields a spun yarn. Subsequently, the resulting spun yarn was subjected to dry heat drawing at 230 °C to a total draw ratio of 16 (the residence time in the dry heat drawing machine was 30 seconds), to recover a PVA/PAN blend fiber of a total 2,000 denier and 1,000 filaments. The fiber had a strength of 10.1 g/d and a Young's modulus of 190 g/d, wherein the PVA was the sea component and the PAN was the islands component. The microscopic examination of the cross section of the fiber indicated that a part of particles of a diameter larger than 0.4 μm had voids, on the periphery, in common to adjacent particles, as shown in Fig. 2.

[0061] The fiber then cut into pieces of a length of 2 mm was dispersed in water, followed by beating by means of the mixer for 5 minutes. The resulting beaten solution was observed with an optical microscope. Most of the fibers were fibrillated into a fibril of a size of about 1 μm. Further, the filtered water time of the beaten solution after the 5-min beating was measured to be 250 seconds. The fiber beatability defined by the present invention was within 2 minutes. The dispersibility of the beaten solution was excellent, with no formation of any fiber ball due to the tangle of fibrils to each other. By cutting the fiber of the present Example into 3-mm pieces, and beating the pieces by means of a refiner followed by paper making, a paper of a higher density and a higher strength was produced.

[0062] Crimping the fiber produced in the Example and cutting the resulting fiber into 51-mm pieces to produce a staple, carding the staple yields a card web, which was then subjected to a high-pressure water jet process at 80 kg/cm². Scanning electron microscopic observation of the surface of the resulting nonwoven fiber indicated that most of the fibers were fibrillated to a fibril of a size C of about 1 μm. Using the nonwoven fabric to wipe the stain of a pair of glasses or on the front
glass of an automobile, the stain was very cleanly wiped off. No problem developed even after washing the nonwoven fabric in water, so the fabric could be used as a wiper in a repeated fashion. Furthermore, the fiber was added to natural rubber followed by kneading to fibrillate the fiber for molding into a sheet. The fiber was more sufficiently fibrillated and more homogeneously dispersed in the rubber than the fiber of Example 1. The resulting sheet had a higher strength than that of Example 1.

Example 5

Fibers were produced in the same manner as in the present Example, except that the final extraction bath was changed to a bath comprising methanol alone or a bath comprising MIBK alone. The fibers had almost the same strength and Young’s modulus as follows; a strength of 9.8 g/d and a Young’s modulus of 180 g/d (for methanol bath) or a strength of 9.7 g/d and a Young’s modulus of 175 g/d (for MIBK bath). However, their beatability was as low as about 20 minutes.

Example 6

A fiber was produced in the same manner as in Example 3, except that the final substitution bath was changed to a bath comprising methanol/MIBK/water (=22/66/12). The observation of the cross section of the resulting fiber clearly showed that the PVA was the sea while the PMMA was the islands, wherein voids were present in at least part of the boundaries with the sea component on the periphery of a part of the islands of a particle size larger than 0.2 μm, in between the sea component and the island components, and that most of the particles of a particle diameter larger than 0.4 μm in particular, had voids in common to adjacent particles. The strength of the fiber was 8.3 g/d, and the Young’s modulus thereof was 170 g/d. The beatability of the fiber was 4.5 minutes, and the filtered water time after 5-min beating was 80 seconds, never involving any fiber ball formation.
vention sheet, wrapping materials of pesticides, pots for seeding growth, and underlining paper of pots for seeding growth; various protection sheets such as fume prevention mask and dust prevention mask, laboratory gown, and dust preventive clothes; various sheets for civil engineering and building, such as house covers, drain material, filtering material, separation material, overlay, roofing, tuft and carpet base cloth, dew prevention sheet, wall interior material, soundproof or vibration-proof sheet, wood-like board, and curing sheet; and various automobile interior sheet, such as floor mat and truck mat, molded ceiling material, head rest, and lining cloth; and the like.

Claims

1. A readily fibrillatable fiber according to any of claims 1 to 6, thereby fibrillating the fiber.

2. A readily fibrillatable fiber according to claim 1, wherein the polymer (B) is a polymer with no water swelling.

3. A readily fibrillatable fiber according to claim 1, wherein the polymer (B) is an acrylonitrile polymer.

4. A readily fibrillatable fiber according to claim 1, wherein the polymer (B) is a poly(methyl methacrylate) polymer.

5. A fiber according to any of claims 1 to 4, wherein the filtered water time after 5-min beating is 75 seconds or more.

6. A readily fibrillatable fiber according to any of claims 1 to 5, wherein voids are present, on the periphery of a part of the island components of a diameter larger than 0.4 μm, in common to adjacent islands.

7. A fibril produced from the fiber according to any of claims 1 to 6.

8. A method for producing a nonwoven fabric, comprising applying high-pressure water jet of 30 kg/cm² or more to a web at least partially containing the fiber according to any of claims 1 to 6, thereby fibrillating the fiber.
9. A method for producing a fiber-reinforced molded article, comprising adding and mixing the fiber according to any of claims 1 to 6 into any one of rubber, plastics and cement, thereby simultaneously fibrillating the fiber.

10. A method for producing a readily fibrillatable fiber, comprising dissolving a vinyl alcohol polymer (A) and a vinyl polymer (B) as defined in claims 1 to 4 in an organic solvent and keeping the weight ratio of A:B in the range of 80/20 to 42/58 to prepare a spinning solution, wet spinning or dry-jet wet spinning the resulting spinning stock solution into a solidifying bath of a mixture of a solidifying solvent having the solidifying potency of the two polymers and the organic solvent of the spinning solution, removing the organic solvent of the spinning solution from the fiber in an extraction bath, and drawing the resulting yarn, provided that the following conditions "I" to "III" should be met:

I. the spinning solution is of a phase separation structure in which particles of a particle size of 2 to 50 μm, comprising the solution of the polymer (B), are present in the solution of the polymer (A);
II. the solidifying solvent is an organic solvent and the solidifying bath includes the organic solvent of the spinning solution at 15 to 75 % by weight; and
III. the total draw ratio is 8 or more.

11. A method for producing a readily fibrillatable fiber according to claim 10, wherein the final substitution bath is a bath comprising three components of alcohols, ketones and water.

Patentansprüche

1. Leicht fibrillierbare Faser mit einem See-Inseln-Querschnitt, umfassend ein Vinylalkoholpolymer (A) das 70 Mol % oder mehr Vinylalkoholeinheiten enthält und ein Vinylpolymer (B) das im wesentlichen keine Vinylalkoholeinheiten enthält, wobei die Komponente (A) die See-Komponente und die Komponente (B) die Insel-Komponente ist und das Gewichtsverhältnis (A)/(B) im Bereich von 80/20 bis 42/58 liegt und wobei Hohlräume im Randbereich eines Teils der Insel-Komponente im Faserquerschnitt vorhanden sind, dadurch gekennzeichnet, daß die Faser eine Stärke von 6 g/d oder mehr und eine Schlagbarkeit (beatability) von 30 Minuten oder weniger aufweist.

2. Leicht fibrillierbare Faser gemäß Anspruch 1, wobei das Polymer (B) ein in Wasser nicht quellbares Polymer ist.

3. Leicht fibrillierbare Faser gemäß Anspruch 1, wobei das Polymer (B) ein Acrylnitrilpolymer ist.

4. Leicht fibrillierbare Faser gemäß Anspruch 1, wobei das Polymer (B) ein Poly(methylmethacrylat)polymer ist.

5. Faser gemäß einem der Ansprüche 1 bis 4, wobei die Wasserfilterzeit nach fünfminütigem Schlagen 75 Sekunden oder mehr beträgt.

6. Leicht fibrillierbare Faser gemäß einem der Ansprüche 1 bis 5, wobei im Randbereich eines Teils der Insel-Komponente Hohlräume vorhanden sind, die einen Durchmesser von mehr als 0,4 μm aufweisen und angrenzenden Inseln gemeinsam sind.

7. Fibrille, hergestellt aus der Faser gemäß einem der Ansprüche 1 bis 6.

8. Verfahren zur Herstellung eines Vlieses, umfassend die Einwirkung eines Hochdruckwasserstrahls von 30 kg/cm² oder mehr auf ein Netzwerk, das zumindest teilweise die Faser gemäß einem der Ansprüche 1 bis 6 enthält, wobei die Faser fibrilliert wird.

9. Verfahren zur Herstellung eines faserverstärkten Formteils, umfassend die Zugabe und das Vermischen der Faser gemäß einem der Ansprüche 1 bis 6 in ein Material, ausgewählt aus Kautschuk, Kunstharzen und Bindemitteln, wobei gleichzeitig die Faser fibrilliert wird.

10. Verfahren zur Herstellung einer leicht fibrillierbaren Faser, umfassend das Auflösen eines Vinylalkoholpolymers (A) und eines Vinylpolymers (B) wie in Ansprüchen 1 bis 4 definiert in einem organischen Lösungsmittel, wobei das Gewichtsverhältnis von (A)/(B) im Bereich 80/20 bis 42/58 gehalten wird, um so eine Spinnlösung herzustellen, Naßspinnen oder Trockenstrahl-Naßspinnen der entstehenden Spinnvorratslösung in ein Fällbad bestehend aus einer Mischung einer Fällflüssigkeit, die gegenüber den zwei Polymeren verfestigende Eigenschaften hat und dem organischen Lösungsmittel der Spinnlösung, Entfernen des organischen Lösungsmittels aus der Spinnlösung von der Faser in einem Abscheidebad, und Strecken des entstehenden Gars unter Maßgabe der folgenden Bedingungen (I) bis (III):

(I) die Spinnlösung zeigt eine phasengetrennte Struktur, in der Partikel in einer Partikelgröße von 2 bis 50 μm, umfassend die Lösung des Polymers (B), in der Lösung des Polymers (A) vorhanden sind;
(II) die Fällflüssigkeit ist ein organisches Lö-
sungsmittel und das Fällbad enthält das organische Lösungsmittel der Spinnlösung in einer Menge von 15 bis 75 Gew.-%; (III) das gesamte Streckverhältnis beträgt 8 oder mehr.

11. Verfahren zur Herstellung einer leicht fibrillierbaren Faser gemäß Anspruch 10, wobei das zuletzt durchlaufene Austauschbad ein Bad ist, das die drei Komponenten Alkohole, Ketone und Wasser umfaßt.

Revendications

1. Fibre aisément fibrillable dont la section transversale possède une structure du type "îles-dans-la-mer", comprenant un polymère d'alcool vinylique (A) contenant des unités d'alcool vinylique à concurrence de 70 moles % ou plus et un polymère vinylique (B) ne contenant essentiellement pas d'unités d'alcool vinylique, dans laquelle le composant (A) représente le composant correspondant à la mer et le composant (B) représente le composant correspondant aux îles, et le rapport pondéral A/B se situe dans le domaine de 80/20 à 42/58, et dans laquelle des vides sont présents à la périphérie d'une partie du composant correspondant aux îles dans la section transversale de la fibre, caractérisée en ce que la fibre possède une résistance de 6 g/d ou plus et une aptitude au raffinage de 30 minutes ou moins.

2. Fibre aisément fibrillable selon la revendication 1, dans laquelle le polymère (B) est un polymère qui ne gonfle pas dans l'eau.

3. Fibre aisément fibrillable selon la revendication 1, dans laquelle le polymère (B) est un polymère d'acrylonitrile.

4. Fibre aisément fibrillable selon la revendication 1, dans laquelle le polymère (B) est un polymère de polyméthacrylate de méthyle.

5. Fibre aisément fibrillable selon l'une quelconque des revendications 1 à 4, dans laquelle les temps requis pour obtenir de l'eau filtrée après raffinage pendant 5 minutes s'élève à 75 secondes ou plus.

6. Fibre aisément fibrillable selon l'une quelconque des revendications 1 à 5, dans laquelle des vides sont présents, à la périphérie d'une partie des composants correspondant aux îles dont le diamètre est supérieur à 0,4 μm, en commun avec ceux d'îles adjacentes.

7. Fibrille fabriquée à partir de la fibre selon l'une quel-

8. Procédé de fabrication d'un non-tissé, comprenant le fait d'appliquer un jet d'eau sous haute pression de 30 kg/cm² ou plus sur une bande contenant au moins en partie la fibre selon l'une quelconque des revendications 1 à 6 pour ainsi fibriller la fibre.

9. Procédé de fabrication d'un article moulé renforcé par des fibres, comprenant le fait d'ajouter et de mélanger la fibre selon l'une quelconque des revendications 1 à 6, soit à du caoutchouc, soit à une matière plastique, soit à du ciment tout en fibrillant la fibre de manière simultanée.

10. Procédé de fabrication d'une fibre aisément fibrillable, comprenant le fait de dissoudre un polymère d'alcool vinylique (A) et un polymère vinylique (B) tels que définis dans les revendications 1 à 4, dans un solvant organique et le fait de maintenir le rapport pondéral A/B dans le domaine de 80/20 à 42/58 pour préparer une solution de filature, le fait de soumettre à une filature au mouillé ou à une filature au mouillé accompagnée d'un séchage par jet d'air la solution concentrée de filature résultante dans un bain de gélification d'un mélange d'un solvant de gélification ayant la capacité de gélifier les deux polymères et du solvant organique de la solution de filature, le fait d'éliminer de la fibre le solvant organique de la solution de filature dans un bain d'extraction et le fait d'étirer le fil resultant en respectant les conditions "I" à "III" ci-après: I. la solution de filature présente une structure du type à séparation de phases dans laquelle des particules possédant une granulométrie de 2 à 50 μm, comprenant la solution du polymère (B), sont présentes dans la solution du polymère (A); II. le solvant de gélification est un solvant organique et le bain de gélification englobe le solvant organique de la solution de filature à concurrence de 15 à 75% en poids; et III. le rapport d'étirage total s'élève à 8 ou plus.

11. Procédé de fabrication d'une fibre aisément fibrillable selon la revendication 10, dans lequel le bain de substitution final est un bain comprenant trois composants, plus précisément des alcools, des cétones et de l'eau.