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(54) **METHOD FOR PRODUCING COMBINED FILAMENT YARN, MIXED FILAMENT YARN, AND METHOD FOR PRODUCING WOVEN FABRIC OR KNITTED FABRIC**

(57) [Problem to be solved] Methods for producing a fiber blended yarn, and a woven fabric or a knit fabric that allow producing fiber-reinforced resin molded bodies having arbitrary shapes and excellent strength are provided.

[Solution] A method for producing a fiber blended yarn of the present invention is a method for producing a fiber blended yarn including at least a thermoplastic resin fiber and a reinforcing fiber, the method including the step of blending the thermoplastic resin fiber and the reinforcing fiber with an interlace method that uses a gas under the presence of a liquid. A fiber blended yarn of

the invention is a fiber blended yarn including at least a thermoplastic resin fiber and a reinforcing fiber, the fiber blended yarn including at least two kinds of organic materials, and the at least two kinds of organic materials adhere to both the reinforcing fiber and the thermoplastic resin fiber. A method for producing a woven fabric or a knit fabric of the invention is a method for producing a woven fabric or a knit fabric including at least a thermoplastic resin and a reinforcing fiber, the method including weaving the reinforcing fiber that comprises a moisture ratio ranging from 0.1 to 5 mass %.

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Description

Technical Field

5 **[0001]** The invention relates to a method for producing a fiber blended yarn, a fiber blended yarn, and a method for producing a woven fabric or a knit fabric.

Background Art

10 **[0002]** Composite material molded bodies made of a resin material with a reinforcing material, such as a glass fiber or a carbon fiber added thereto, are used for structural parts of various machines and automobiles, pressure vessels, and tubular structures, etc. Such composite material molded bodies are demanded to conform to an arbitrary shape in order to achieve light weight and high strength at the same time.

15 **[0003]** As a material forming such composite material molded bodies, a uniformly commingled continuous fiber blended yarn obtained by mixing a reinforcing fiber and a thermoplastic resin fiber using a fluid, and a fabric cloth made from such a fiber blended yarn have been proposed (see, for example, Patent Literature 1). In order to increase impregnation ability of the fiber blended yarn during molding, fiber blending conditions have been studied mainly for increasing a fiber blend rate (a degree of commingling of the fibers) (see, for example, Patent Literature 2). Further, unlike common organic fibers, the reinforcing fiber tend to be fluffed due to damages, and therefore require precise control of conditions for opening and mixing the fibers (see, for example, Patent Literature 3). It is also known that, when the reinforcing fiber is processed in a highly humid environment, the reinforcing fiber less tends to be bulky, that is, the reinforcing fiber less tends to be opened (see, for example, Patent Literature 4).

20 **[0004]** As described above, during manufacturing of a fiber blended yarn using the reinforcing fiber, moisture removal has been performed during fiber blending in view of suppressing damages to the reinforcing fiber and increasing the fiber blend rate. Further, it has been technical common knowledge that the fibers are handled in a dry atmosphere in view of suppressing adsorption of moisture, which will be impeditive during a process of obtaining molded bodies by heating the fiber blended yarn.

Citation List

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Patent Literature

[0005]

35 [Patent Literature 1] Japanese Unexamined Patent Publication No. H2-112916
[Patent Literature 2] Japanese Unexamined Patent Publication No. H3-275729
[Patent Literature 3] Japanese Unexamined Patent Publication No. H4-222246
[Patent Literature 4] Japanese Unexamined Patent Publication No. S59-43141

40 Summary of Invention

Technical Problem

45 **[0006]** However, conventionally known fiber blended yarns and fabric cloths have been developed mainly for preventing damages to the reinforcing fiber during fiber blending and improving the fiber blending state to increase impregnation ability during molding. In order to apply fiber blended yarns and fabric cloths to structural materials, such as automobile materials, higher strength of the fiber blended yarns and fabric cloths is demanded.

Solution to Problem

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[0007] The present inventors have found, through intensive study to solve the above-described problems in the prior art, that, by performing fiber blending of the thermoplastic fiber and the reinforcing fiber using a gas in the presence of a liquid, the resulting molded bodies exhibit high strength and high interface strength, thereby achieving the present invention.

55 **[0008]** Namely, the method for producing a fiber blended yarn of the present invention is a method for producing a fiber blended yarn comprising at least a thermoplastic resin fiber and a reinforcing fiber, the method comprising the step of blending the thermoplastic resin fiber and the reinforcing fiber with an interlace method that uses a gas under the presence of a liquid.

[0009] It is preferred that the reinforcing fiber contain a liquid in an amount of 300 mass % or less.

[0010] It is preferred that the interlace method be a fluid disturbance method.

[0011] It is preferred that the reinforcing fiber comprise a water soluble component in an amount ranging from 0.1 to 5 mass % relative to the reinforcing fiber.

[0012] It is preferred that the reinforcing fiber comprise a hydrophilicity index of 8 degrees or more.

[0013] Another aspect of the method for producing a fiber blended yarn of the invention is a method for producing a fiber blended yarn comprising at least a thermoplastic resin fiber and a reinforcing fiber, the method comprising a step of blending the fibers with an interlace method that uses a gas after a step of treating the thermoplastic resin fiber and/or the reinforcing fiber with a liquid.

[0014] It is preferred that the liquid contain an organic material.

[0015] It is preferred that a rate of change of surface tension of the thermoplastic resin fiber when the organic material in an amount of 10 mass % relative to the thermoplastic resin fiber is mixed be 30% or less.

[0016] It is preferred that a liquid that is collected during the step of blending the fibers with the interlace method be mixed with the liquid that is used in the step of treating with the liquid.

[0017] The fiber blended yarn of the invention is a fiber blended yarn comprising at least a thermoplastic resin fiber and a reinforcing fiber, the fiber blended yarn comprising at least two kinds of organic materials, and the at least two kinds of organic materials adhere to both the reinforcing fiber and the thermoplastic resin fiber.

[0018] It is preferred that a degree of dispersion of the organic materials over surfaces of the reinforcing fiber and the thermoplastic resin fiber be 5% or more.

[0019] It is preferred that the fiber blended yarn comprise a degree of flexibility of 20 degrees or more.

[0020] It is preferred that the fiber blended yarn comprise a void ratio of 20% or more.

[0021] It is preferred that a total amount of the organic materials be less than 2 mass % relative to the fiber blended yarn.

[0022] The method for producing a woven fabric or a knit fabric of the invention is a method for producing a woven fabric or a knit fabric comprising at least a thermoplastic resin and a reinforcing fiber, the method comprising weaving the reinforcing fiber that comprises a moisture ratio ranging from 0.1 to 5 mass %.

Advantageous Effects of Invention

[0023] According to the method for producing a fiber blended yarn, the fiber blended yarn, and the method for producing a woven fabric or a knit fabric of the present invention, a fiber blended yarn, a woven fabric, and a knit fabric that allow producing fiber-reinforced resin molded bodies having arbitrary shapes and excellent strength can be obtained.

Brief Description of the Drawings

[0024]

[FIG. 1] FIG. 1 is a schematic view for explaining Taslan processing,

[FIG. 2] FIG. 2 is a schematic view showing a state where fiber blended yarns are wound around an aluminum die frame used in Examples, and

[FIG. 3] FIG. 3 is a schematic view showing a die used in the Examples.

Description of Embodiments

[0025] Now, the present invention will be described in detail. The following description is not intended to limit the invention, and various modifications can be made to the invention within the spirit and scope of the invention.

Fiber blended yarn

[0026] A fiber blended yarn of the present invention refers to a yarn comprising at least a reinforcing fiber and a thermoplastic resin fiber. The reinforcing fiber and/or the thermoplastic resin fiber is preferably a multifilament fiber in view of the strength and ease of handling of the yarn. Each single filament of the multifilament fiber of the reinforcing fiber may partially be cut; however, a reinforcing fiber bundle is preferably continuous in view of the strength. The thermoplastic resin fiber may be in any form; however, it is preferably a continuous fiber in view of the stability of the fiber blending process.

[0027] How the reinforcing fiber and the thermoplastic resin fiber are mixed is not particularly limited, and these fibers may be paralleled, filaments of the respective fibers may be commingled, one of the fibers may cover around the other of the fibers, or these fibers may be twisted together, for example. In order to increase impregnation ability during molding and imparting high strength, it is preferred that filaments of the respective fibers be only partially commingled. Since a

lower degree of commingling results in a more straight reinforcing fiber and thus the reinforcing fiber tends to exhibit higher strength, having a minimum amount of commingled portions allows quick impregnation starting from such portions. A commingling ratio of the reinforcing fiber is preferably in the range from 0.1 to 20%, more preferably in the range from 0.2 to 15%, and even more preferably in the range from 0.3 to 10%. The degree of commingling is defined by a ratio of filaments of the reinforcing fiber adjacent to filaments of the thermoplastic resin fiber relative to the total number of filaments in the reinforcing fiber bundle, and is calculated by observing 20 cross sections at arbitrary positions of the fiber blended yarn.

[0028] A volume ratio of the reinforcing fiber to the thermoplastic resin fiber in a fiber blended yarn is preferably in the range from 50 to 900 vol.%, more preferably in the range from 66 to 400 vol.%, and even more preferably in the range from 81 to 233 vol.%, in view of achieving high strength and clean appearance.

[0029] The fiber blended yarn of the invention includes at least two kinds of organic materials, and the at least two kinds of organic materials adhere to both the reinforcing fiber and the thermoplastic resin fiber. When both the reinforcing fiber and the thermoplastic resin fiber have the at least two kinds of organic materials in common, affinity between these fibers is increased, and thus provides effects of ease of handling as a yarn, and increased impregnation ability during molding. In view of facilitating enhancement of these effects, it is preferred that at least one of the organic materials is water soluble. Further, if the total amount of the organic materials is excessively large, ease of handling may be lowered, and therefore the total amount of the organic materials relative to the fiber blended yarn is preferably less than 2 mass %, more preferably not more than 1.7 mass %, even more preferably not more than 1.4 mass %, and most preferably not more than 1.1 mass %.

[0030] The number of types of the organic materials adhering to the fiber blended yarn can be calculated by liquid chromatography mass spectrometry using an appropriate solvent to extract the organic materials from the fiber blended yarn. In order to find the amounts of the organic materials adhering to the reinforcing fiber and the thermoplastic resin fiber in the fiber blended yarn, the reinforcing fiber and the thermoplastic resin fiber are separated from the fiber blended yarn, and the respective fibers are water-extracted, and then are solvent-extracted to quantitate the amount of water soluble components and the amount of non-water soluble components. Further, by performing NMR measurement on the extracts, sources of the components can be found, that is, the extracts can be separated into a component (A) contained in the raw material reinforcing fiber, a component (B) contained in the raw material thermoplastic resin fiber, and a component (C) contained in a liquid used during the fiber blending. It is preferred that both the reinforcing fiber and the thermoplastic resin fiber contain the components (A) and (B) in view of the impregnation property during molding and imparting strength.

[0031] These organic materials adhering to the surfaces of the reinforcing fiber and the thermoplastic resin fiber are preferably dispersed at a degree of dispersion of 5% or more in view of the impregnation ability during molding and increasing a final interface strength in the resulting molded bodies. The degree of dispersion is more preferably 10% or more, and even more preferably 15% or more. The degree of dispersion can be calculated as follows. The organic materials are extracted from the fiber blended yarn and the mass of the organic materials is measured, and then a ratio of the mass of the organic materials to the mass of the fiber blended yarn is calculated. This measurement is performed similarly at arbitrary 20 points to calculate an average value and a standard deviation, and a value obtained by dividing the standard deviation by the average value is found as the degree of dispersion.

[0032] In view of ease of handling during weaving, knitting, or braiding of the fiber blended yarn, the fiber blended yarn preferably has a degree of flexibility of 20 degrees or more, more preferably 40 degrees or more, even more preferably 60 degrees or more, and most preferably 80 degrees or more. The degree of flexibility of the fiber blended yarn is determined by: cutting a 20 cm-long piece of the fiber blended yarn; making a ring of the fiber blended yarn by fixing one end of the yarn to the other end the yarn using a tape having a width of 1.5 cm; suspending the ring of the fiber blended yarn vertically with supporting the yarn at the tape-fixed portion (at this time, if the fiber blended yarn does not become vertical, making it vertical lightly using the hands); then, vertically inverting the ring of the yarn supported at the tape-fixed portion such that the fiber blended yarn vertically stands with the tape-fixed portion positioned below; holding the fiber blended yarn for one minute without touching the yarn; and measuring an angle of the collapsed fiber blended yarn relative to the vertical direction. If the fiber blended yarn is bent and there are two angles, a larger angle is found as the degree of flexibility.

[0033] In view of the balance between ease of handling during a process, such as weaving, knitting, or braiding, of the fiber blended yarn and ease of handling of the fiber blended yarn in the form of a woven fabric, a knit fabric, or a braided fabric, it is preferred that the degree of flexibility of the fiber blended yarn is changeable depending on moisture absorption by the yarn. An amount of change of the degree of flexibility of the fiber blended yarn before and after moisture absorption is preferably 30 degrees or more, more preferably 40 degrees or more, and even more preferably 50 degrees or more.

[0034] In view of ease of handling of the fiber blended yarn during weaving, knitting, or braiding, and suppressing damages to the fiber blended yarn during handling, it is preferred that the fiber blended yarn include voids in it, and a void ratio is preferably 20% or more, more preferably 25% or more, and even more preferably 30% or more. The void

ratio can be found by wrapping the fiber blended yarn in a shrink tube, pouring and hardening a colored epoxy resin in the tube, and cutting and polishing the cross-section to observe the cross-section.

$$\text{Void ratio} = \text{Area of voids} / \text{Area within outer perimeter of fiber blended yarn} \times 100$$

[0035] The area of voids is an area of the colored epoxy resin within the outer perimeter of the fiber blended yarn, and the outer perimeter of the fiber blended yarn refers to a figure drawn by connecting the outermost filaments of the yarn.

[0036] The fiber blended yarn may include components other than the reinforcing fiber, the thermoplastic resin fiber, and the organic materials. Depending on environment in which the resulting molded bodies are used, it is preferred to add an antioxidant, an ultraviolet absorber, a colorant, a heat-transfer agent, a heat stabilizing agent, or the like.

Method for producing fiber blended yarn

[0037] The fiber blended yarn of the invention is produced by blending the reinforcing fiber and the thermoplastic resin fiber using a gas in the presence of a liquid. The liquid as used herein refers to a material that is liquid under temperatures and pressures of processing conditions. The type of the liquid may be selected as appropriate depending on the processing conditions, and water, an organic solvent, or the like, can be used as appropriate. Water is particularly preferable in view of the stability. The gas as used herein refers to a material that is gaseous immediately before contacting the reinforcing fiber and/or the thermoplastic resin fiber. The type of the gas may be selected as appropriate depending on the processing conditions, and air, steam, an organic gas, or the like, may be used as appropriate. Air is preferred in view of the stability.

[0038] By positively adding the liquid, damages to the reinforcing fiber during the fiber blending can be suppressed, and, even in a state where the degree of mixing of the fibers is low, the reinforcing fiber can quickly be impregnated with a resin during molding, resulting in high tensile strength and interface strength. The amount of the liquid is not particularly limited, and can appropriately be adjusted depending on types of the reinforcing fiber and the thermoplastic resin used, a single filament diameter, fineness, etc. The liquid may be added in the form of steam or liquid. The liquid is preferably added in the form of liquid in view of the impregnation ability during molding and strength of the resulting molded bodies. While it is sufficient that one of the reinforcing fiber and the thermoplastic resin fiber is moisturized, it is preferred that at least the reinforcing fiber be moisturized, and it is more preferred that both the reinforcing fiber and the thermoplastic resin fiber be moisturized. Since it is preferred that the reinforcing fiber and the thermoplastic resin fiber be moisturized before the fiber blending, a moisturizing step is preferably included immediately before the fiber blending. It is not necessary that both the reinforcing fiber and the thermoplastic resin fiber are subjected to the moisturizing step in order to moisturize them. For example, the reinforcing fiber may be subjected to the moisturizing step, and then, the reinforcing fiber and the thermoplastic resin fiber may be paralleled, thereby making the liquid on the reinforcing fiber to migrate onto the thermoplastic resin fiber.

[0039] It is preferred that the liquid contain an organic material. During the moisturizing step, the liquid may contain a different type of organic material from an organic material contained in the liquid. As the former organic material, it is preferred to add an organic material that imparts the reinforcing fiber and the thermoplastic resin fiber with a property that is difficult to be originally imparted thereto, such as one increasing affinity between the reinforcing fiber and the thermoplastic resin fiber, one imparting hydrophilicity to suppress generation of static electricity, one imparting a color or a function, such as flame resistance, heat resistance, or weather resistance, to the resulting molded bodies, or one promoting fiber opening of the reinforcing fiber during molding to increase impregnation action. Taking the residual efficiency of the organic material on the fiber blended yarn after the fiber blending process into account, the organic material is preferably fine-dispersed in the liquid, and is more preferably in the state of emulsion which is a water dispersion.

[0040] In order to have the impregnation ability and high physical properties in a short-time molding, the organic material is preferably one that results in a rate of change of surface tension of the thermoplastic resin fiber of 30% or less, more preferably 20% or less, even more preferably 15% or less, and most preferably 10% or less, when the organic material in an amount of 10 mass % relative to the thermoplastic resin fiber is mixed.

[0041] A difference between the surface tension of the organic material and the surface tension of the thermoplastic resin fiber is preferably less than 22, more preferably less than 17, even more preferably less than 12, and most preferably less than 7. The surface tension is measured at a temperature higher by 45°C than the higher one of the melting points of the organic material and the thermoplastic resin fiber.

[0042] In order to impart good physical properties after the impregnation, a difference between the SP value (solubility parameter) of the thermoplastic resin fiber and the SP value of the organic material is preferably less than 3 (cal/cm³), more preferably less than 2, even more preferably less than 1.5, and most preferably less than 1.

[0043] Particularly preferred examples of the organic material that meet the above-described specifications include polymers or oligomers of the same family as the thermoplastic resin fiber. The "same family" as used herein means that

the organic material has the same functional group as that the repeating unit of the thermoplastic resin fiber has. For example, in the case where the thermoplastic resin fiber is made of polyamide 66, an organic material having an amide bond is preferably applied.

[0044] In view of controlling the amount of the organic material to be added, the moisturizing step is preferably effected by a method where a liquid containing the organic material is sprayed and the excessive liquid is collected, or a method where immersion is performed in a circulating liquid and the concentration of the organic material in the circulating liquid is controlled. During the fiber blending process using a gas, the excessive organic material is collected together with the excessive liquid, and it is preferred that the collected materials be recycled in the moisturizing step.

[0045] The moisture content is not particularly limited, and a moisture content that allows obtaining the above-described effects may be selected as appropriate. However, in view of increasing the productivity and minimizing the waste liquid, the moisture content relative to the reinforcing fiber is preferably not more than 300 mass %, more preferably not more than 250 mass %, even more preferably not more than 200 mass %, and most preferably not more than 150 mass %. The moisture content can be found by stopping the production line in a state where the process is stable, cutting a portion just before entering the fiber blending process and measuring the weight of the portion, and then, removing the liquid from the portion and measuring the weight of the portion.

[0046] The interface shear stress of the reinforcing fiber in the fiber blended yarn preferably changes relative to the interface shear stress of the raw material reinforcing fiber, and changes more preferably by 5% or more, even more preferably by 10% or more, and most preferably by 15% or more relative to the interface shear stress of the raw material reinforcing fiber. The interface shear stress can be changed by making components, such as a sizing agent, adhering to the reinforcing fiber migrate due to the liquid. The interface shear stress can be measured using a microdroplet method.

[0047] A method for reeling the reinforcing fiber can be selected as appropriate, and examples thereof include reeling from inside, reeling from outside, and roll reeling. In view of suppressing damages to the yarn in the yarn path, it is preferred that the reinforcing fiber be moisturized before the reeling. The reinforcing fiber may be kept in the moisturized state when the reinforcing fiber is produced and coated with a sizing agent, or may be moisturized before the reinforcing fiber is used. The moisturization may be achieved by immersing the reinforcing fiber in a predetermined liquid, by spraying a liquid using an atomizer, or the like, or by holding the reinforcing fiber in high humidity for a predetermined time. In a case where it is difficult to use the reinforcing fiber in the moisturized state, roll reeling, which allows reeling the reinforcing fiber without twisting the reinforcing fiber, is preferred. The moisture content during reeling is not particularly limited; however, the reinforcing fiber immediately after the reeling preferably has a degree of flexibility of 5 degrees or more, more preferably 10 degrees or more, and even more preferably 15 degrees or more. The degree of flexibility can be measured in the same manner as the above-described degree of flexibility of the fiber blended yarn.

[0048] The fiber blending can be achieved by using a known method depending on the structure of the fiber blended yarn, and some fiber blending processes may be used in combination. Now, a method for producing a fiber blended yarn of the reinforcing fiber and the thermoplastic resin fiber, or a fiber blended yarn comprising mixed filaments of the reinforcing fiber and the thermoplastic resin fiber, which is a preferred aspect of the fiber blended yarn, is described.

[0049] For example, a fiber opening and yarn doubling method, wherein fiber opening is performed using an external force, such as pressure produced by an electrostatic force or fluid spraying, or pressure produced by pressing with a roller, and then yarn doubling or paralleling is performed in the state where the reinforcing fiber and the thermoplastic resin fiber are opened; and an interlace method using a fluid are usable. The interlace method using a fluid, which allows removing excessive liquid while blending the fibers using a gas, is preferably used. The interlace method using a fluid is a method where the fibers are interlaced through the action of the fluid, and examples thereof include a disturbance method using a fluid and an interlace method (wherein air is blown in a direction transverse to the yarn). In a case where a carbon fiber, which is easily damaged by an external force applied from a lateral side, is used as the reinforcing fiber, the fluid disturbance method is preferably used, and the Taslan (R) method, wherein air is blown in the same direction as the direction of travel of the yarn, is particularly preferably used. A thickness of and the number of filaments in a raw material reinforcing fiber bundle are adjusted as appropriate, and the production conditions are also adjusted as appropriate.

[0050] Now, the Taslan processing, which is a preferred aspect of the invention, is described. The Taslan processing is a technique which binds the filaments fed as core filaments and float filaments into a bulky looped yarn with forces of air. For example, as shown in FIG. 1, when the core filaments and the float filaments fed by rotation of rollers pass through a nozzle mounted in a Taslan box, the filaments are disturbed by the forces of air and bound together. The core filaments are filaments forming the core of a Taslan yarn, and the float filaments are densely looped around the core filaments. It is usually preferred that a feeding rate of the float filaments by rollers be set higher than a feeding rate of the core filaments by rollers. The nozzle is mainly composed of a housing and a core, and air jets are applied from holes called orifices provided in the core to bind the filaments together.

[0051] Although it does not matter which of the reinforcing fiber and the thermoplastic resin fiber forms the core filaments or the float filaments, it is preferred that the reinforcing fiber be used as the core filaments and the thermoplastic resin fiber be used as the float filaments in view of the strength. In view of the strength and the productivity of the fiber

blended yarn, a yarn speed is preferably in the range from 10 to 1000 m/minute, more preferably in the range from 20 to 700 m/minute, even more preferably in the range from 30 to 500 m/minute, and most preferably in the range from 50 to 300 m/minute.

[0052] In view of improving the strength of the resulting molded bodies by increasing the straightness of the yarn, the reinforcing fiber is fed at a rate preferably in the range from 0 to 10%, more preferably in the range from 0.1 to 5%, even more preferably in the range from 0.2 to 3%, and most preferably in the range from 0.3 to 1.8% of the yarn speed. The feeding rate of the thermoplastic resin fiber may be adjusted arbitrarily in view of adjusting the entwined state with the reinforcing fiber, and is preferably in the range from 1 to 15%, more preferably in the range from 2 to 10%, even more preferably in the range from 3 to 7%, and most preferably in the range from 4 to 6%. The ratio of the feeding rate of the float filaments relative to the feeding rate of the core filaments is preferably in the range from 100 to 600%, more preferably in the range from 110 to 500%, and even most preferably in the range from 150 to 400%. In view of suppressing damages to the reinforcing fiber, achieving an adequate interlace state, and adequately blowing off the liquid, the air pressure is preferably in the range from 0.5 to 10 kgf/cm², more preferably in the range from 1 to 5 kgf/cm², and even more preferably in the range from 1.5 to 3 kgf/cm². Before entering the Taslan box, the reinforcing fiber and/or the thermoplastic resin fiber is moisturized, and the liquid is blown off while the fiber blending is performed using air, thereby controlling the moisture content.

Water soluble component

[0053] It is preferred that the fiber blended yarn of the invention contain a water soluble component. The "water soluble component" as used herein refers to a compound that has a solubility of 10 g or more in 100 g of water at 23°C. For example, water soluble polymers, such as polyvinylpyrrolidone, polyethylene glycol, and derivatives and copolymers thereof, polyacrylic acid, polysulfonic acid, polyvinyl alcohol, polyvinylacetamide, cellulose derivatives, starch derivatives, etc., and low molecular weight compounds having a reactive functional group, such as epoxy resin, and acrylate resin, are preferably used.

[0054] The water soluble component may be contained in the reinforcing fiber and/or the thermoplastic resin fiber in the fiber blended yarn. In a case where both the reinforcing fiber and the thermoplastic resin fiber contain the water soluble component, increased adhesion between these fibers is achieved, which preferably facilitates impregnation during molding. Further, it is preferred that the water soluble component be non-uniformly adhering to surfaces of the reinforcing fiber in view of increasing the interface strength between the reinforcing fiber and the thermoplastic resin forming a matrix in the resulting molded body. In view of the balance between the impregnation ability and the interface strength, the water soluble component is contained in an amount preferably in the range from 0.1 to 5 mass %, more preferably in the range from 0.3 to 4 mass %, even more preferably in the range from 0.5 to 3 mass %, and most preferably in the range from 1 to 2 mass % relative to the reinforcing fiber.

[0055] The water soluble component may be added to the raw materials, may be added when the fiber blending is performed, or may be added after the fiber blended yarn is produced. In view of facilitating the non-uniform adhesion to the surfaces of the reinforcing fiber, it is preferred that the water soluble component be added to the raw material reinforcing fiber. In the case where the reinforcing fiber contains the water soluble component, the water soluble component contacting the liquid during the fiber blending process migrates due to the liquid. With this, the water soluble component is distributed over the surfaces of the reinforcing fiber, and also migrates onto the thermoplastic resin fiber.

Reinforcing fiber

[0056] As the reinforcing fiber, those commonly used in molded bodies of reinforcing fiber composite materials can be used, and preferred examples thereof include, but are not limited to, at least one selected from the group consisting of glass fiber, carbon fiber, aramid fiber, ultra-high strength polyethylene fiber, polybenzazole-based fiber, liquid crystal polyester fiber, polyketone fiber, metal fiber, and ceramic fiber. Glass fiber, carbon fiber, and aramid fiber are preferred in view of the mechanical physical properties, thermal properties, and versatility, and carbon fiber is preferred in view of the elasticity.

[0057] A single filament diameter of the reinforcing fiber is not particularly limited; however, the single filament diameter is preferably in the range from 1 to 22 μm , more preferably in the range from 3 to 17 μm , and even more preferably in the range from 5 to 12 μm in view of the strength and ease of handling of the resulting molded bodies. The number of filaments in a reinforcing fiber bundle may be set as appropriate depending on ease of handling, and a reinforcing fiber bundle of 3,000 filaments, 6,000 filaments, 12,000 filaments, or 24,000 filaments may preferably be used.

[0058] A sizing agent is preferably used with the reinforcing fiber, and also a coupling agent for forming interfaces between the reinforcing fiber and the thermoplastic resin, a binder for improving ease of handling of the reinforcing fiber and assisting formation of interfaces between the thermoplastic resin and the coupling agent, a lubricant for improving ease of handling of the reinforcing fiber, etc., are preferably used.

[0059] The sizing agent changes the condition of the surfaces of the reinforcing fiber. It is preferred that the reinforcing fiber have high affinity to the liquid used in the fiber blending process in view of the strength of the fiber blended yarn and strength of the resulting molded bodies. The state where "the reinforcing fiber has high affinity to the liquid" refers to such a state that, when the reinforcing fiber bundle is cut into a piece having a length of about 5 cm and put in a bath of the liquid, the reinforcing fiber bundle is spread into fibers.

[0060] It is preferred that the sizing agent be applied in the form of a liquid or gas in view of achieving uniform application to the reinforcing fiber. In a case where a compound having high melting and boiling points is used, the sizing agent may be applied while being heated, or may be dissolved in a solvent to be applied. As other components, an antioxidant, an ultraviolet absorber, a colorant, a heat-transfer agent, a heat stabilizing agent, etc., may be included.

[0061] The type of the sizing agent may be selected using an interface strength with the matrix resin that is found according to a microdroplet test as described, for example, in Japanese Unexamined Patent Publication No. 2015-67926. However, since the sizing agent may be volatilized or altered due to heat, it is preferred that the test is conducted after the sizing agent is subjected to a heat history during molding. It is preferred to use the previously described water soluble component as the sizing agent.

[0062] The lubricant contributes to improving adjustability of and prevention of damages to the reinforcing fiber, and improving fiber openability. As the lubricant, any of common liquid or solid lubricative materials suitable for the purpose can be used, and examples thereof include, but are not limited to, one or more selected from: animal, vegetable, or mineral waxes, such as carnauba wax and lanolin wax; and surfactants, such as fatty acid amide, fatty acid ester, fatty acid ether, aromatic ester, and aromatic ether.

[0063] The binder contributes to improving binding and the interface adhesion strength of the reinforcing fiber. As the binder, a polymer or a thermoplastic resin suitable for the purpose can be used. Examples of the polymer include, but are not limited to, thermosetting resins, such as: epoxy resins, such as bisphenol A epoxy resin; phenol resins obtained by reacting various phenols with formalin; urea resins obtained by reacting urea with formalin; and melamine resins obtained by reacting melamine with formalin. Further, polyurethane resins, such as one synthesized from an isocyanate (such as m-xylylene diisocyanate, 4,4'-methylene bis(cyclohexyl isocyanate), and isophorone diisocyanate) and a polyester or polyether diol can also be used favorably.

[0064] The thermoplastic resin used as the binder is not particularly limited, and examples thereof include polyolefin resin, polyamide resin, polyacetal resin, polycarbonate resin, polyester resin, polyether ketone, polyether ether ketone, polyether sulfone, polyphenylene sulfide, thermoplastic polyether imide, thermoplastic fluorine resin, and modified thermoplastic resins obtained by modifying the above-listed resins. Using the same type of thermoplastic resin and/or modified thermoplastic resin as the thermoplastic resin fiber forming the fiber blended yarn is preferred in view of improving the adhesion between the reinforcing fiber and the thermoplastic resin fiber of the resulting composite material molded bodies.

[0065] In view of increasing the efficiency of the fiber blending process, the reinforcing fiber used in the invention has a hydrophilicity index of preferably 8 degrees or more, more preferably 30 degrees or more, and even more preferably 60 degrees or more. The hydrophilicity index as used herein is a unique index for compatibility to the fiber blending process of the invention. The hydrophilicity index is found by performing a measurement which is similar to that for finding the degree of flexibility of the fiber blended yarn in a dry state and a wet state, as shown in Examples, and calculating a difference between measurement values obtained in these states.

Thermoplastic resin fiber

[0066] As the thermoplastic resin fiber, fibers made of matrix resins commonly used in composite materials can be used. Preferred examples thereof include continuous fibers obtained by melting and spinning at least one thermoplastic resin selected from: polyolefin resins, such as polyethylene, polypropylene; polyamide resins, such as polyamide 6, polyamide 66, polyamide 46; polyester resins, such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate; polyacetal resins, such as polyoxymethylene; polycarbonate resins; polyether ketone; polyether ether ketone; polyether sulfone; polyphenylene sulfide; thermoplastic polyether imide; thermoplastic fluorine resins, such as tetrafluoroethylene-ethylene copolymer; and modified thermoplastic resins obtained by modifying these resins.

[0067] Among these thermoplastic resins, polyolefin resins, polyamide resins, polyester resins, polyether ketone, polyether ether ketone, polyether sulfone, polyphenylene sulfide, thermoplastic polyether imide, and thermoplastic fluorine resins are preferred. In view of the mechanical physical properties and versatility, polyolefin resins, modified polyolefin resins, polyamide resins, and polyester resins are more preferred. Further, in view of the thermal physical properties, polyamide resins and polyester resins are even more preferred. Still further, in view of the durability against repeated load, polyamide resins are still more preferred, and aliphatic polyamide resins, in particular, polyamide 6 and polyamide 66 can favorably be used.

[0068] The thermoplastic resin fiber may contain a lubricant, an antioxidant, an ultraviolet absorber, a colorant, a heat-transfer agent, a heat stabilizing agent, etc., and it is preferred to add a compound having high affinity to the liquid used

during the fiber blending in view of increasing the fiber blending efficiency, and increasing the impregnation ability by sharing this compound with the reinforcing fiber.

Woven fabric, knit fabric

[0069] It is preferred that the fiber blended yarn of the invention be processed into a fabric to use the fabric as an intermediate material for obtaining fiber-reinforced resin molded bodies. The form of the fabric is not particularly limited, and examples thereof may include a unidirectional reinforced material wherein the fiber blended yarns are paralleled in a certain direction, a fabric cloth using a composite yarn, for example, a woven fabric or a knit fabric, lace, felt, a non-woven fabric, a film or a plate-like body, etc. As the intermediate material, a flexible unidirectional reinforced material, a woven fabric, a knit fabric, lace, felt, and a non-woven fabric are preferred in view of the shape conformity to the die in manufacturing of the fiber-reinforced resin molded bodies, a knit fabric, a unidirectional reinforced material, and a woven fabric are more preferred in view of less bends and higher strength of the reinforcing fiber, and a knit fabric and a woven fabric are even more preferred in view of the shape stability.

[0070] The woven fabric may be a biaxial woven fabric or a triaxial woven fabric. The type of weave of the woven fabric is not particularly limited, and examples thereof may include plain weave, twill weave, sateen weave, leno weave, and gauze weave.

[0071] In view of the strength of the resulting fiber-reinforced resin molded bodies, twill weave, which results in lower crimp ratio of the reinforcing fiber, is more preferred.

[0072] As the knit fabric, for example, a so-called non-crimp fabric, i.e., a multi-axial warp-knitted fabric is preferred in view of the strength, and examples of the stitch of the knit fabric may include tricot, combination, etc.

Weaving or knitting process

[0073] The method used to obtain the intermediate material in the form of fabric is not particularly limited, and can be selected depending on the use and the purpose.

[0074] For example, the woven fabric is obtained using a loom, such as a shuttle loom, a rapier loom, an air jet loom, or a water jet loom, and at least partially contains the fiber blended yarn. As a preferred example, the woven fabric may be obtained by inserting weft yarns through warp yarns of fibers including the fiber blended yarn. In view of stably obtaining the woven fabric with suppressed damages to the reinforcing fiber, a rapier loom is preferably used. In order to stabilize the tension of the woven fabric to facilitate obtaining the woven fabric having uniform quality, the width of the rapier loom is preferably 60 cm or more, more preferably 80 cm or more, and even more preferably 100 cm or more. While the quality is stabilized when the width is above a certain value, it is preferred to determine the width as appropriate in view of ease of use depending on the yarn used. In a case where a glass fiber or a carbon fiber is used in the reinforcing fiber bundle, the width is preferably not more than 6 m, more preferably not more than 5 m, even more preferably not more than 4 m, and most preferably not more than 3 m.

[0075] The knit fabric can be produced using a knitting machine, such as a latch needle circular knitting machine, a flatbed knitting machine, a tricot knitting machine, or a raschel knitting machine, to knit fibers that at least partially include the composite yarn.

[0076] The non-woven fabric can be obtained by forming a sheet-like collection of fibers called "web" of fibers at least partially including the composite yarn, and then bonding the fibers by using a physical action, such as using a needlepunching machine, a stitchbonding machine, or a columnar jet flow machine, by using a thermal action, such as using an emboss roll, or by using an adhesive.

[0077] With respect to other forms of the intermediate material, etc., the method described in Japanese Unexamined Patent Publication No. 2015-101794 can be used as appropriate.

[0078] In the invention, it is preferred that the process of obtaining the woven fabric or the knit fabric be performed in a state where the reinforcing fiber is moisturized. By handling the reinforcing fiber in the moisturized state, fluff can be prevented, and the straightness of the reinforcing fiber in the woven fabric or knit fabric can be increased, thereby increasing the strength of the molded body. In view of the relationship between the strength and the ease of handling, the moisture ratio is preferably in the range from 0.1 to 5 mass %, more preferably in the range from 0.2 to 4 mass %, and even more preferably in the range from 0.3 to 3 mass % relative to the reinforcing fiber.

[0079] The timing of the moisturization of the reinforcing fiber is not limited, and may be during the process of producing the fiber blended yarn, or during spooling the produced fiber blended yarn, or a moisturization step may be performed separately after the produced fiber blended yarn has been spooled. Further, the moisturization may be performed during warping as a preparation step for weaving or knitting, during reaching-in or drawing-in, or immediately before insertion of weft yarns. In view of the strength and the impregnation ability, it is preferred that the reinforcing fiber be moisturized before the fiber blended yarn is produced, and the moisture amount be adjusted during the fiber blending before weaving or knitting.

[0080] In the invention, after the woven fabric or knit fabric is produced, the fabric can be immersed in a liquid to increase the impregnation ability, and also to increase the interface strength and the strength of the resulting molded bodies. The fabric in this stage may include only the reinforcing fiber, or the reinforcing fiber and a thermoplastic resin. The thermoplastic resin may be in the form of powder, film, woven fabric, or fiber. The thermoplastic resin in the form of powder or fiber is preferred in view of reducing a distance to the reinforcing fiber, and the thermoplastic resin in the form of fiber is preferred in view of the stability of the fabric. The thermoplastic resin in the form of fiber may be blended in advance with the reinforcing fiber, or may be in the form of a mixed woven fabric or a mixed knit fabric with the reinforcing fiber. The state of the reinforcing fiber can be adjusted as appropriate by lightly squeezing the reinforcing fiber after the fiber is immersed in the liquid.

Molding method

[0081] A fiber-reinforced resin molded body can be produced using the above-described fiber blended yarn or the intermediate material as a forming material. It should be noted that the method for producing a fiber-reinforced resin molded body is not limited to one described below, and various methods can be applied.

[0082] For example, a base material (preferably in the form of a woven fabric or a knit fabric) to form a fiber-reinforced resin molded body is cut according to a desired molded body, and a necessary number of sheets of the base material suitable for the thickness of the final product are stacked, and the stack is set to conform to the shape of a die. At this time, using the above-described intermediate material allows increasing the degree of freedom with respect to the die comparing to conventional common composite plates made of a reinforcing fiber impregnated with a resin, and molding with high degree of freedom in shape can be achieved even when the design of molded body includes differences in level. A step of drying the base material may be included before the base material is set in the die. The drying step may be performed before and/or after the cutting.

[0083] The sheets of the base material may be cut one by one, or a stack of a desired number of sheets of the base material may be cut. In view of the productivity, it is preferred to cut a stack of sheets of the base material. The cutting may be achieved using any method, and examples thereof may include a water jet, a blade press machine, a hot blade press machine, a laser, and a plotter.

[0084] After the base material is set in the die, the die is closed and compressed. Then, the temperature of the die is controlled to a temperature equal to or higher than the melting point of the thermoplastic resin forming the fiber-reinforced resin molded body to melt and shape the thermoplastic resin. The die compression pressure is not particularly limited; however, it is preferably 1 MPa or more, and more preferably 3 MPa or more.

[0085] A hybrid molded body may be produced with the process for producing a fiber-reinforced resin molded body, wherein the intermediate material is set in the die and the die is closed and compressed, and a predetermined thermoplastic resin composition is injected into the die after a predetermined time and molded in the die, such that the thermoplastic resin fiber and the predetermined thermoplastic resin composition are joined.

Use application

[0086] The fiber-reinforced resin molded body is favorably applicable to structural materials for aircrafts, automobiles, construction materials, sports goods, etc.

[0087] Examples of application to automobiles may include, but are not limited to, a chassis/frame, underside parts, driving system parts, interior parts, exterior parts, functional parts, and other parts.

Examples

[0088] Specific examples of the present invention and comparative examples are shown below, which are not intended to limit the invention.

Carbon fiber (CF)

Carbon fiber A (CF-A)

[0089] 2.9 mass % of polyvinylpyrrolidone (water soluble component) was adhered as a sizing agent to a PAN (polyacrylonitrile) carbon fiber having a standard elasticity with a single filament diameter of 7 μm , a filament number of 12000, and a density of 1.81 g/cm^3 . The fiber was immersed in water to remove the sizing agent to separate it into filaments and a tensile test was conducted on a 5 cm-long piece, and a fracture load was found to be 6.2 g. That is, the strength of the fiber bundle was calculated to be about 2,000 MPa. The hydrophilicity index was 80.

Carbon fiber B(CF-B)

[0090] 0.11 mass % of bisphenol A polyethylene glycol ether (an average repeating unit number of the polyethylene glycol was 9.3), which is a water soluble component, and 0.1 mass % of a long-chain hydrocarbon compound, which is a non-water soluble component, were adhered as a sizing agent to a PAN (polyacrylonitrile) carbon fiber having a standard elasticity with a single filament diameter of 7 μm , a filament number of 12000, and a density of 1.81 g/cm^3 . The strength of the fiber bundle was 4,500MPa, and the hydrophilicity index was 12.

Carbon fiber C (CF-C)

[0091] A carbon fiber was prepared in the same manner as the carbon fiber A except that the amount of polyvinylpyrrolidone in the sizing agent was 0.08 mass %. The hydrophilicity index was 50.

Thermoplastic resin fiber

[0092] LEONA® 470/144BAU (available from Asahi Kasei Fibers Co., Ltd.) having a fineness of 470 dtex and a filament number of 144 was used, which contained 0.9% of water soluble components.

Method for molding unidirectional material

[0093] Test pieces were obtained according to the procedure shown below with a target width of 20mm, a target length of 200mm, and a target thickness of 1mm. Two test pieces (molded bodies) were obtained by one molding process. The molding machine used was a hydraulic molding machine (available from Shoji Co., Ltd.) having a maximum die compression force of 50 tons.

[0094] As shown in FIG. 2, the fiber blended yarns were wound around an aluminum die frame. The aluminum die frame had a thickness of 5mm, and the number of winding turns was a minimum number with which a total sectional area of the fiber blended yarns of not less than 20 mm^2 was achieved. The die frame with the fiber blended yarns was set in a die as shown in FIG. 3 including a COR (core) and a CAV (cavity) with a clearance of 0.5 mm.

[0095] The interior of the molding machine was heated to a temperature of 300°C, and the die was installed therein. Then, the die was compressed with a die compression force of 5 MPa to effect compression molding. The molding time was 10 minutes from when the melting point of the main component of the matrix resin (e.g., 265°C if the main component was polyamide 66) was reached, and then the die was quenched and opened to remove the molded bodies.

Method for molding woven fabric

[0096] As the molding machine, a hydraulic molding machine (available Shoji Co., Ltd.) with a maximum die compression force 50 tons was used.

[0097] A stack of a predetermined number of sheets of the woven fabric cut to a length of 9.5 cm and a width of 19.5 cm was charged in a die having a length of 10 cm, a width of 20 cm, and a thickness of 2 mm. It should be noted that the number of sheets was a minimum number with which a volume of 40 cm^3 or more of the woven fabric was achieved.

[0098] The interior of the molding machine was heated to a temperature of 300°C, and the die was installed therein. Then, the die was compressed with a die compression force of 5 MPa to effect compression molding. The molding time was 10 minutes from when the melting point of the main component of the matrix resin (e.g., 265°C if the main component was polyamide 66) was reached, and then the die was quenched and opened to remove the molded bodies.

Tensile strength, tensile elasticity, and strength development ratio of unidirectional material

[0099] The test pieces were vacuum dried at 80°C for two days before tests. Tabs made of a glass fiber reinforced resin (GFRP) having a thickness of 2 mm, a width of 20 mm, and a length of 50 mm were attached with an instant glue to both ends of each test piece such that a distance between the tabs was 100 mm. A strain gauge (KFGS-5-120-C1-23 available from Kyowa Electronic Instruments Co., Ltd.) was attached at the center of the test piece to be measured.

[0100] Tensile tests were performed at a tensile speed of 1 mm/minute using a 100 kN tensile tester available from Instron and a dynamic strain gauge available from Kyowa Electronic Instruments Co., Ltd. The maximum load was found as a tensile strength (MPa), and the maximum slope of a strain-load curve was found as a tensile elasticity.

[0101] A measured value of tensile strength relative to a theoretical strength calculated according to the equation below was found as a strength development ratio of the unidirectional material.

Theoretical strength = Tensile strength of reinforcing fiber bundle $\times$ Volume ratio of reinforcing fiber + Tensile strength of resin $\times$ Volume ratio of resin

Tensile strength, tensile elasticity, and strength development ratio of woven fabric

[0102] The test pieces were vacuum dried at 80°C for two days before tests. Each test piece was cut into a dumbbell shape (having a length of 100 mm, a length of parallel portion of 6 mm, and a thickness of 2 mm). Tabs made of a glass fiber reinforced resin (GFRP) having a thickness of 2 mm, a width of 13 mm, and a length of 22.5 mm were attached with an instant glue to both ends of each test piece such that a distance between the tabs was 50 mm. A strain gauge (KFGS-5-120-C1-23 available from Kyowa Electronic Instruments Co., Ltd.) was attached at the center of the test piece to be measured.

[0103] Tensile tests were performed at a tensile speed of 1 mm/minute using a 10 kN tensile tester available from Instron and a dynamic strain gauge available from Kyowa Electronic Instruments Co., Ltd., in 0-90 degrees directions. The maximum load was found as a tensile strength (MPa), and the maximum slope of a strain-load curve was found as a tensile elasticity.

[0104] A measured value of tensile strength relative to a theoretical strength calculated according to the equation below was found as a strength development ratio. A composite material has higher strength in the direction of fibers and lower strength in the direction perpendicular to the fibers. In the examples of the invention and the comparative examples, the density of the warp yarns and the density of the weft yarns were the same, and therefore a half value of the unidirectional material was found as the theoretical strength of the tensile strength of the woven fabric.

Theoretical strength = Tensile strength of reinforcing fiber bundle $\times$ Volume ratio of reinforcing fiber + Tensile strength of resin $\times$ Volume ratio of resin / 2

Volume fraction of reinforcing fiber

[0105] Measurements were performed according to the burning method defined in JIS K7075.

Un-impregnation ratio

[0106] Five cross-sections at arbitrary positions were cut from the molded body and embedded in epoxy resin, and were polished with care so as not to break the reinforcing fiber. Observation was performed using a microscope, and areas occupied by the fiber bundle, the thermoplastic resin, and voids, respectively, were found from the obtained images to calculate a ratio of the area of voids relative to the entire area. The measurement was performed for four points per cross-section, and a median value of data for the total of 20 points was found as the un-impregnation ratio.

Amount of water soluble components in reinforcing fiber, thermoplastic fiber, and fiber blended yarn

[0107] The fibers in an amount of 3.5 g were collected and immersed in 60 ml of pure water, and heated at 80°C for 8 hours. Then, filtration was performed, and washing with 40ml of pure water was performed twice. All the liquids were collected and mixed to be used as an analyte solution, and the analyte solution was freeze-dried to collect the components dissolved therein. The mass of the collected components was measured to quantitate the amount of water soluble components.

Amount of components adhering to reinforcing fiber and thermoplastic resin fiber in fiber blended yarn

[0108] The fiber blended yarn was cut into a suitable length and the reinforcing fiber and the polyamide fiber were completely separated therefrom. Water extraction was performed on each of the fibers to quantitate the amount of water soluble components adhering thereto. Thereafter, ratios of a component (A) originated from the reinforcing fiber and a component (B) originated from the polyamide fiber were calculated and quantitated using NMR. It should be noted that the amount of components adhering to the reinforcing fiber was shown in mass percent relative to the reinforcing fiber, and the amount of components adhering to the thermoplastic fiber was shown in mass percent relative to the thermoplastic fiber.

[0109] However, with respect to Example 2, of which the raw material reinforcing fiber contained a non-water soluble

component, extraction using chloroform was conducted after the water extraction to perform quantitation in the similar manner, and the amount of the non-water soluble component was added to the amount of the water soluble components.

[0110] Further, an organic component (C) was added to the liquid only in Example 8. With respect to the reinforcing fiber, the organic component (C) was extracted using hexafluoro-2-propanol and quantitated. With respect to the polyamide fiber, a weight per length was measured, and an increase relative to the raw materials was found as the amount of the organic component (C).

Commingling ratio of reinforcing fiber in fiber blended yarn

[0111] The degree of commingling is defined by a ratio of the number of filaments of the reinforcing fiber adjacent to filaments of the thermoplastic resin fiber relative to the total number of the filaments in the reinforcing fiber bundle. The fiber blended yarn wrapped in a shrink tube was cut, and the cross sections were observed using an optical microscope to calculate the ratio by image processing. The total of 20 cross sections at arbitrary positions were observed and an average value was calculated.

Void ratio of fiber blended yarn

[0112] The fiber blended yarn was wrapped in a shrink tube, a colored epoxy resin was injected and hardened in the tube, and then cut and polished to observe the cross section.

$$\text{Void ratio} = \text{Area of voids} / \text{Area within outer perimeter of fiber blended yarn} \times 100$$

[0113] The area of voids is an area of the colored epoxy resin within the outer perimeter of the fiber blended yarn, and the outer perimeter of the fiber blended yarn refers to a figure drawn by connecting the outermost filaments of the yarn.

Degree of dispersion of organic material

[0114] The organic materials were extracted from the fiber blended yarn using a solvent and the mass of the organic materials was measured, and then a ratio of the mass of the organic materials to the mass of the fiber blended yarn was calculated. This measurement was performed similarly at arbitrary 20 points to calculate an average value and a standard deviation, and a value calculated by dividing the standard deviation by the average value was found as the degree of dispersion.

Degree of flexibility of fiber blended yarn, and hydrophilicity index of reinforcing fiber

[0115] The degree of flexibility of the fiber blended yarn was determined by: cutting a 20 cm-long piece of the fiber blended yarn immediately after produced; making a ring of the fiber blended yarn by fixing one end of the yarn to the other end the yarn using a tape having a width of 1.5 cm; suspending the ring of the fiber blended yarn vertically with supporting the yarn at the tape-fixed portion (at this time, if the fiber blended yarn did not become vertical, making it vertical lightly using the hands); then, vertically inverting the ring of the yarn supported at the tape-fixed portion such that the fiber blended yarn vertically stood with the tape-fixed portion positioned below; holding the fiber blended yarn for one minute without touching the yarn; and measuring an angle of the collapsed fiber blended yarn relative to the vertical direction. When the fiber blended yarn was bent and there were two angles, a larger angle was found as the degree of flexibility. This measurement was performed at arbitrary 20 points, and an average value was calculated.

[0116] The hydrophilicity index of the reinforcing fiber was found by performing a measurement which is similar to that for finding the degree of flexibility of the fiber blended yarn in a dry state and a wet state, and calculating a difference between measurement values obtained in these states. The hydrophilicity index in the dry state was measured after vacuum drying at 25°C for 2 hours. The hydrophilicity index in the wet state was found by preparing a sheet of KIMTOWEL (available from Nippon Paper Industries Co., Ltd.) folded in four on which 50 ml of distilled water was uniformly sprayed, placing a sample that had been measured in the dry state in the KIMTOWEL and keeping it still for 10 seconds without applying a load, and thereafter performing the measurement.

Surface tension, rate of change of surface tension

[0117] Measurements were performed using a contact angle measurement instrument, DM500, available from Kyowa Interface Science Co., Ltd., according to a suspension method (Laplace method). Since the melting point of the polyamide

66 is 265°C, the measurement was performed one minute after the formation of a droplet at 310°C in nitrogen atmosphere. The melt density was calculated as 1 g/cc. Since this measurement had to be performed in a sufficiently dry state, the polyamide 66 was vacuum dried at 90°C for two days as a pretreatment for the measurement.

[0118] In the polyamide 66 (thermoplastic resin fiber), an organic material in an amount of 10 mass % relative to the polyamide 66 was mixed using a twin-screw extruder under low shear conditions. The surface tension was measured in the same manner to calculate a rate of change of the surface tension.

Measurement of interface shear stress

[0119] Measurements were performed according to a microdroplet test using a composite material interface property evaluation equipment HM410 (available from Tohei Sangyo Co., Ltd.)

[0120] A single filament was removed from the raw material reinforcing fiber or the reinforcing fiber in the fiber blended yarn, and set on the composite material interface property evaluation equipment. On the equipment, the thermoplastic resin used as a raw material of the thermoplastic resin fiber was melted to form a droplet on the single filament of the reinforcing fiber, and sufficiently cooled to room temperature to obtain a measurement sample. The measurement sample was again set on the equipment and the droplet was nipped using a blade of the equipment and the single filament of the reinforcing fiber was made to travel at a speed of 0.06 mm/minute on the equipment to measure a maximum pulling load $f(N)$ at which the droplet was pulled out, and an interface adhesion strength τ was calculated according to the equation below:

$$\text{Interface adhesion strength } \tau = f/\pi \cdot R \cdot l,$$

(wherein f is a maximum pulling load (N), R is a diameter (m) of the single filament of the reinforcing fiber, and l is a particle diameter (m) of the droplet in the pulling direction).

[0121] The rate of change of the interface shear stress was found by calculating an absolute percentage value of a difference between an interface shear stress of the reinforcing fiber removed from the fiber blended yarn and an interface shear stress of the raw material reinforcing fiber relative to the interface shear stress of the raw material reinforcing fiber.

Example 1

[0122] One carbon fiber A and ten polyamide fibers were paralleled and passed through flowing water at a flow rate of 45ml/minute, and then passed through rollers and introduced into a Taslan box, where Taslan processing was performed with an air pressure of 2.0 kgf/cm² to obtain a fiber blended yarn. The yarn was spooled at a yarn speed of 65 m/minute, the raw material carbon fiber was fed at 66 m/minute, and the raw material polyamide fibers were fed at 68 m/minute.

Example 2

[0123] A fiber blended yarn was obtained in the same manner as in Example 1 except that the carbon fiber B was used. The non-water soluble component remained on the carbon fiber after the fiber blending.

Example 3

[0124] A fiber blended yarn was obtained in the same manner as in Example 1 except that the amount of water was 85 ml/minute.

Example 4

[0125] A fiber blended yarn was obtained in the same manner as in Example 1 except that the number of the polyamide fibers was six.

Example 5

[0126] One carbon fiber A and ten polyamide fibers were paralleled and passed through flowing water at a flow rate of 45ml/minute, and then introduced into an interlace nozzle (KC-AJI-L, having a diameter of 1.5 mm, propulsion-type, available from KYOCERA Corporation), and a fiber blended yarn was obtained at an air pressure of 0.5 kg/cm² and a

processing speed of 50 m/minute.

Example 6

- 5 **[0127]** The fiber blended yarn obtained in Example 1 was introduced in a water bath and spooled to reduce the amount of polyvinylpyrrolidone to 0.08 mass %.

Example 7

- 10 **[0128]** The carbon fiber A was used after left for three days at a humidity of not more than 95%. Further, during production of the fiber blended yarn, 30ml of water was sprayed using an atomizer at intervals of 1.5 minutes to moisturize a carbon fiber bobbin. One carbon fiber A was passed through flowing water at a flow rate of 30 ml/minute. Thereafter, the carbon fiber and ten polyamide fibers were paralleled and introduced into a Taslan box, where Taslan processing was performed with an air pressure of 2.0 kgf/cm² to obtain a fiber blended yarn. The yarn was spooled at a yarn speed of 65 m/minute, the raw material carbon fiber was fed at 66 m/minute, and the raw material polyamide fibers were fed at 68 m/minute.

Example 8

- 20 **[0129]** A fiber blended yarn was obtained in the same manner as in Example 7 except that a polyamide emulsion (SEPOLSION PA200, available from Sumitomo Seika Chemicals Co., Ltd.) diluted five times was used in place of the flowing water.
[0130] The surface tension of the polyamide 66 was 29.9 mN/m, the surface tension of solids in the polyamide emulsion was 35 mN/m, the surface tension of a mixture obtained by mixing the solids of the polyamide emulsion and the polyamide 66 was 31.0 mN/md, and a rate of change of the surface tension was 3.7%.
 25 **[0131]** The molding time was one minute from when the melting point was reached.

Example 9

- 30 **[0132]** A fiber blended yarn was obtained in the same manner as in Example 1 except that the flow rate of the flowing water was 300ml/minute and the filaments were introduced into the Taslan box immediately after contacting with the flowing water.

Example 10

- 35 **[0133]** A fiber blended yarn was obtained in the same manner as in Example 7 except that the number of the polyamide fibers was 14.

Example 11

- 40 **[0134]** A fiber blended yarn was obtained in the same manner as in Example 1 except that the carbon fiber was dried before used, the yarn was spooled at a speed of 45 m/minute, the carbon fiber was fed at a speed of 46 m/minute, and the polyamide fibers were fed at a speed of 48 m/minute. The operation speed was decreased since the reeling was not smooth.

Comparative Example 1

- 45 **[0135]** A fiber blended yarn was obtained in the same manner as in Example 1 except that the water was not used. Fluff of the CF was generated in the environment.

Comparative Example 2

- 50 **[0136]** One carbon fiber A and ten polyamide fibers were paralleled and spooled without any treatment. Fluff of the CF was generated in the environment.

Comparative Example 3

- 55 **[0137]** The carbon fiber C and ten polyamide fibers were introduced into a Taslan box, where Taslan processing was

performed with an air pressure of 2.0 kgf/cm² to obtain a fiber blended yarn. The yarn was spooled at a yarn speed of 65 m/minute, the raw material carbon fiber was fed at 66 m/minute, and the raw material polyamide fibers were fed at 68 m/minute. Fluff of the CF was generated in the environment.

5 *Comparative Example 4*

10 **[0138]** One carbon fiber A and ten polyamide fibers were paralleled and introduced into a water bath filled with water. The water was circulated with a pump at a flow rate of 20 m/minute to open the fibers with the water flow. The opened fibers were laid together and introduced into a water jet nozzle, where the fibers were blended by turbulent flow of water fed at a rate of 10 kg/cm². The yarn speed was 20 m/minute, and the carbon fiber A and the polyamide fibers were fed at 22 m/minute. The resulting yarn was spooled and dried at 150°C for 10 hours.

Example 12

15 **[0139]** The fiber blended yarn obtained in Example 1 was woven using a rapier loom to obtain a woven fabric of 4/4 twill weave with a density of six yarns/inch. The moisture content of the carbon fiber during the weaving process was 5 mass %.

20 *Comparative Example 5*

[0140] A woven fabric was obtained in the same manner as in Example 12 except that the fiber blended yarn obtained in Comparative Example 3 was used.

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Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Raw materials	Reinforcing fiber	CF-B	CF-A	CF-A	CF-A	Fiber blended yarn obtained in Example 1 was introduced in water bath water bath and spooled and spooled	CF-A	CF-A	CF-A
	10 polyamide fibers	10 polyamide fibers	10 polyamide fibers	6 polyamide fibers	10 polyamide fibers		10 polyamide fibers	10 polyamide fibers	10 polyamide fibers
	Taslan processing	Taslan processing	Taslan processing	Taslan processing	Interlace		Taslan processing	Taslan processing	Taslan processing
	Amount of water soluble components in reinforcing fiber	0.11%	2.9%	2.9%	2.9%		2.9%	2.9%	2.9%
	Amount of water soluble components in thermoplastic resin fiber	0.9%	0.9%	0.9%	0.9%		0.9%	0.9%	0.9%
Fiber blending process	Fiber blending speed	65	65	65	65		65	65	65
	Degree of flexibility of reinforcing fiber before reeling	30	15	30	30		60	60	30
	Water	45 ml/min.	45ml/min.	85 ml/min.	45ml/min.		30ml/min.	30 ml/min.	300 ml/min.
	Moisture ratio during fiber blending	80%	40%	150%	60%		120%	100%	300%
Fiber blended yarn	Commingling ratio	8%	6%	7%	4%	8%	9%	9%	5%

(continued)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Degree of dispersion of organic material	16%	6%	13%	14%	17%	5%	21%	15%	10%
Component A in reinforcing fiber	1.6	0.15	0.97	1.3	1.2	0.08	1.3	0.8	0.5
Component B in reinforcing fiber	0.15	0.14	0.1	0.17	0.14	0.01	0.13	0.07	0.02
Component C in reinforcing fiber	-	-	-	-	-	-	-	1.2	-
Component A in polyamide fibers	0.23	0.02	0.17	0.27	0.24	0.03	0.25	0.05	0.12
Component B in polyamide fibers	0.08	0.08	0.05	0.06	0.07	0.01	0.09	0.01	0.02
Component C in polyamide fibers	-	-	-	-	-	-	-	0.4	-
Degree of flexibility of fiber blended yarn	100	24	86	115	104	68	90	85	70
Void ratio of fiber blended yarn	31	27	25	30	26	25	33	27	24
Rate of change of interface shear stress	30	10	33	29	28	10	35	40	14

(continued)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Molded body	63.2	63.3	60.9	65.1	63.6	58	59	56	62
Volume fraction of reinforcing fiber									
Un-impregnation ratio (%)	0.35	0.03	0.4	0.4	0.8	0.1	0.05	0.01	0.3
Tensile strength	1107	2222	1007	983	910	950	1235	1210	1020
Strength development ratio	86	77	81	74	70	80	102	105	80
Tensile elasticity	126.3	131.9	130.1	131.9	121	126	140	137	125

Table 2

	Example 10	Example 11	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Example 12	Comp. Ex. 5
Raw materials	Reinforcing fiber	CF-A	CF-A	CF-A	CF-C	CF-A		
	14 thermoplastic resin fibers	10 polyamide fibers	10 polyamide fibers	10 polyamide fibers	10 polyamide fibers	10 polyamide fibers		
	Fiber blending process	Taslan processing	Taslan processing	Parallel and spooled	Taslan processing	In water, turbulent flow		
	Amount of water soluble components in reinforcing fiber	2.9%	2.9%	2.9%	0.08%	29%		
	Amount of water soluble components in thermoplastic resin fiber	0.9%	0.9%	0.9%	0.9%	0.9%		
Fiber blending process	Fiber blending speed	65	65	65	65	20		
	Degree of flexibility of reinforcing fiber before reeling	60	30	30	10	30		
	Water	30 ml/min.	45 ml/min.	None	None	In water		
	Moisture ratio during fiber blending	120%	70%	0%	0%	>>500%		
Fiber blended yarn	Commingling ratio	10%	7%	3%	3%	30%		
	Degree of dispersion of organic material	24%	18%	4%	4%	1 %		

Woven fabric made of fiber blended yarn obtained in Comp. Ex. 3

Woven fabric made of fiber blended yarn obtained in Example 1

(continued)

	Example 10	Example 11	Comp. Ex. 1	Comp. Ex. 2	Comp Ex. 3	Comp, Ex. 4	Example 12	Comp. Ex. 5
Component A in reinforcing fiber	1.2	1.7	2.9	2.9	0.08	0		
Component B in reinforcing fiber	0.15	0.15	0	0	0	0		
Component C in reinforcing fiber	-	-	-	-	-	-		
Component A in polyamide fibers	0.26	0.22	0	0	0	0		
Component B in polyamide fibers	0.08	0.09	0.09	0.09	0.9	0		
Component C in polyamide fibers	-	-	-	-	-	-		
Degree of flexibility of fiber blended yarn	110	95	8	6	10	12		
Void ratio of fiber blended yarn	32	31	19	12	17	15		
Rate of change of interface shear stress	32	28	0	0	0	-25		
Volume fraction of reinforcing fiber	46	61	64.1	65.3	62	62	60	60
Un-impregnation ratio (%)	0.04	0.39	8.7	>10	6	1.5	0.34	5.8
Tensile strength	979	1056	620	420	660	800	567	360
Strength development ratio	102	84	47	31	52	63	92	58
Tensile elasticity	135	122	95	80	105	110	55.3	45
Molded body								

[0141] The test pieces of the fiber blended yarns of Examples 1 to 11 exhibited excellent tensile strength, tensile elasticity, and strength development ratio. The woven fabric obtained in Comparative Example 5 generated much fluff, and litter of the carbon fiber in the environment was observed. The woven fabric of Comparative Example 5 exhibited lower tensile strength, tensile elasticity, and strength development ratio than the test piece of the woven fabric of Example 12.

Industrial Applicability

[0142] According to the method for producing a fiber blended yarn, the fiber blended yarn, and the method for producing a woven fabric or a knit fabric of the present invention, an intermediate material that is favorably applicable to reinforced materials for materials required to have high level mechanical physical properties, such as structural parts of various machines, automobiles, etc., can be obtained, and thus the present invention has industrial applicability.

Claims

1. A method for producing a fiber blended yarn comprising at least a thermoplastic resin fiber and a reinforcing fiber, the method comprising the step of blending the thermoplastic resin fiber and the reinforcing fiber with an interlace method that uses a gas under the presence of a liquid.
2. The method for producing a fiber blended yarn as claimed in Claim 1, wherein the reinforcing fiber contains a liquid in an amount of 300 mass % or less.
3. The method for producing a fiber blended yarn as claimed in Claim 1 or 2, wherein the interlace method is a fluid disturbance method.
4. The method for producing a fiber blended yarn as claimed in any one of Claims 1 to 3, wherein the reinforcing fiber comprises a water soluble component in an amount ranging from 0.1 to 5 mass % relative to the reinforcing fiber.
5. The method for producing a fiber blended yarn as claimed in any one of Claims 1 to 4, wherein the reinforcing fiber comprises a hydrophilicity index of 8 degrees or more.
6. A method for producing a fiber blended yarn comprising at least a thermoplastic resin fiber and a reinforcing fiber, the method comprising a step of blending the fibers with an interlace method that uses a gas after a step of treating the thermoplastic resin fiber and/or the reinforcing fiber with a liquid.
7. The method for producing a fiber blended yarn as claimed in Claim 6, wherein the liquid contains an organic material.
8. The method for producing a fiber blended yarn as claimed in Claim 7, wherein a rate of change of surface tension of the thermoplastic resin fiber when the organic material in an amount of 10 mass % relative to the thermoplastic resin fiber is mixed is 30% or less.
9. The method for producing a fiber blended yarn as claimed in any one of Claims 6 to 8, wherein a liquid that is collected during the step of blending the fibers with the interlace method is mixed with the liquid that is used in the step of treating with the liquid.
10. A fiber blended yarn comprising at least a thermoplastic resin fiber and a reinforcing fiber, the fiber blended yarn comprising at least two kinds of organic materials, and the at least two kinds of organic materials adhere to both the reinforcing fiber and the thermoplastic resin fiber.
11. The fiber blended yarn as claimed in Claim 10, wherein a degree of dispersion of the organic materials over surfaces of the reinforcing fiber and the thermoplastic resin fiber is 5% or more.
12. The fiber blended yarn as claimed in Claim 10 or 11 comprising a degree of flexibility of 20 degrees or more.
13. The fiber blended yarn as claimed in any one of Claims 10 to 12 comprising a void ratio of 20% or more.
14. The fiber blended yarn as claimed in any one of Claim 10 to 13, wherein a total amount of the organic materials is

less than 2 mass % relative to the fiber blended yarn.

15. A method for producing a woven fabric or a knit fabric comprising at least a thermoplastic resin and a reinforcing fiber, the method comprising weaving the reinforcing fiber that comprises a moisture ratio ranging from 0.1 to 5 mass %.

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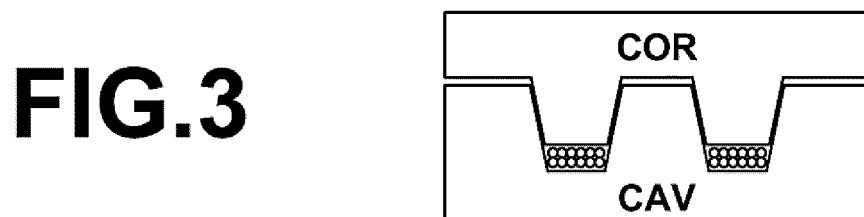
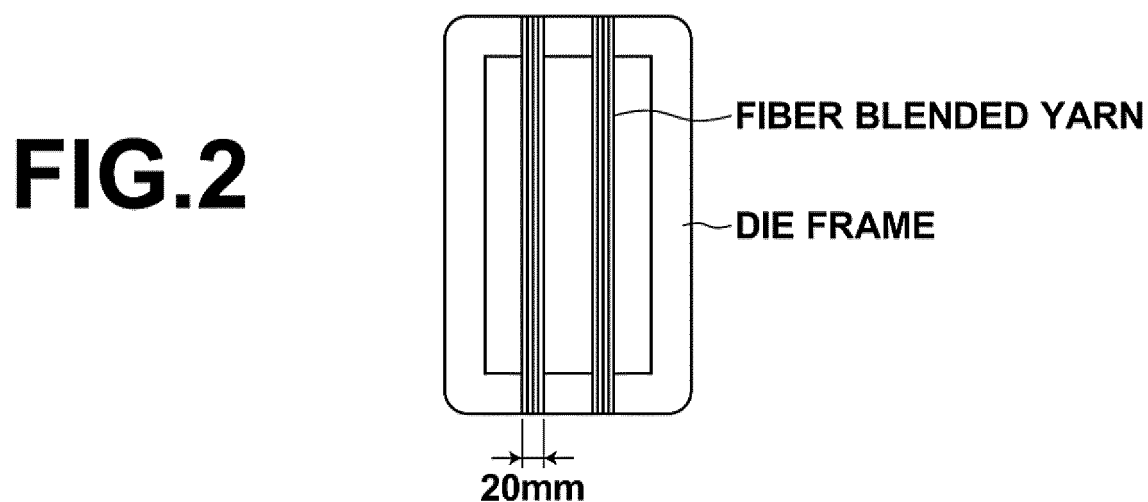
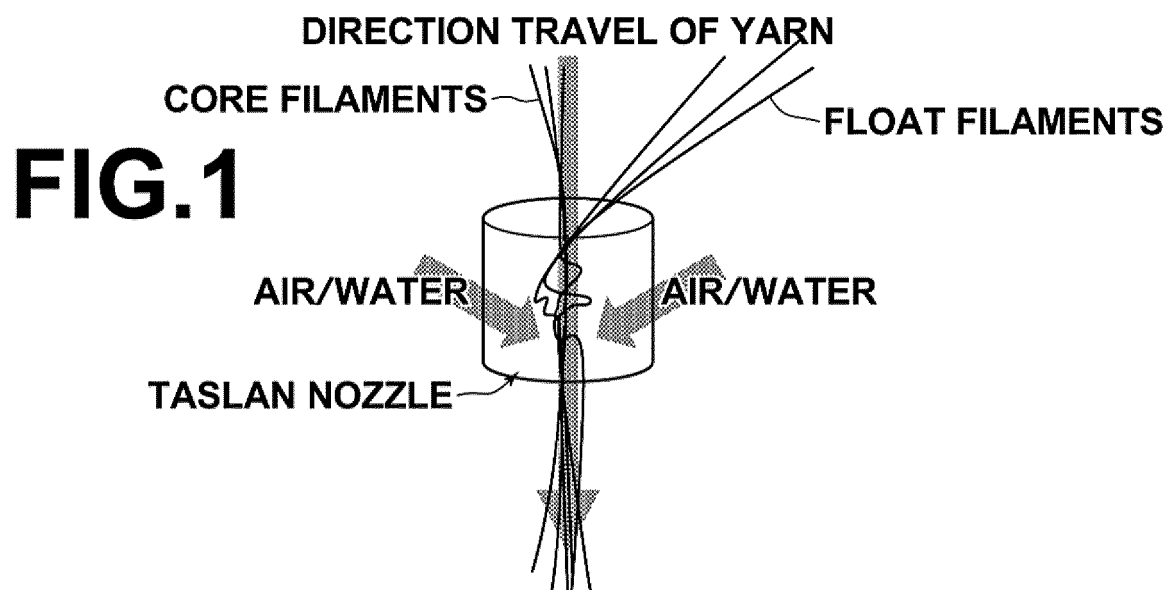
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/024790

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. D02J1/00 (2006.01) i, D02G3/04 (2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. D02J1/00-13/00, D02G1/00-3/48, D03D1/00-27/18, D04B1/00-1/28, D04B21/00-21/20

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 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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.
X Y A	JP 2-91240 A (TOYOBO BOSEKI KABUSHIKI KAISHA) 30 March 1990, claims, page 3, upper right column, line 16 to lower left column, line 4, page 4, upper right column, line 18 to lower left column, line 8, page 5, lower right column, bottom line to page 6, upper left column, line 19 (Family: none)	1-3 4-7 8, 9, 15
X Y	JP 2016-56478 A (GIFU UNIVERSITY) 21 April 2016, claims, paragraphs [0061], [0068], [0069], [0075] & JP 5885223 B1 & US 2017/0260657 A1 & WO 2016/039242 A1 (claims, paragraphs [0096], [0111]-[0114], [0126]) & EP 3192904 A1 & TW 201612371 A & KR 10-2017-0029649 A & CN 106687627 A	10-14 4, 5

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

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"&" document member of the same patent family

Date of the actual completion of the international search
28 September 2018 (28.09.2018)Date of mailing of the international search report
30 October 2018 (30.10.2018)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/024790

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	P 2004-270126 A (TORAY INDUSTRIES, INC.) 30 September 2004, paragraphs [0039], [0040] (Family: none)	6, 7
A	JP 2015-101793 A (ASAHI KASEI CHEMICALS CORP.) 04 June 2015, claims, examples (Family: none)	1-15

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REFERENCES CITED IN THE DESCRIPTION

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- JP S5943141 B [0005]
- JP 2015067926 A [0061]
- JP 2015101794 A [0077]