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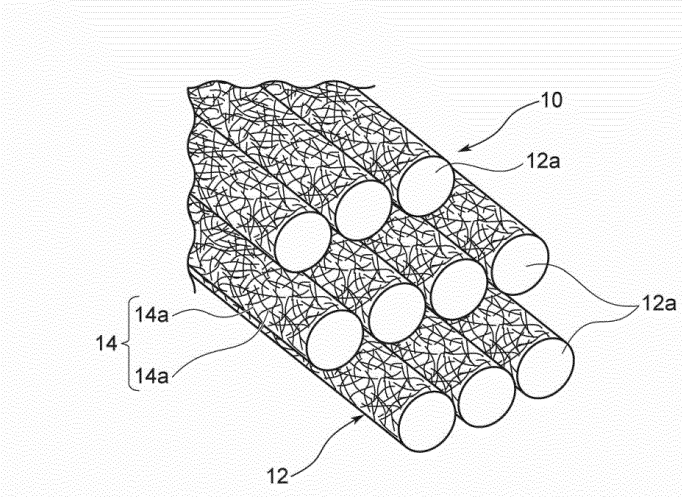
(54) COMPOSITE MATERIAL PRODUCTION METHOD AND COMPOSITE MATERIAL

(57) There are provided a method for producing a composite material (10) from which a high-strength prepreg having CNT-derived properties fully exerted is obtained, comprising a step of immersing a carbon fiber bundle (12) including a plurality of continuous carbon fibers (12a) in a carbon-nanotubes-isolated dispersion containing a plurality of isolatedly-dispersed carbon nanotubes (14a) and applying ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less to form a structure comprising a plurality of carbon nanotubes (14a) on the surface of each of the plurality of carbon fibers (12a), wherein the structures are directly attached to the surface of each of the plurality of carbon fibers (12a) and form together a network structure in which the carbon nanotubes (14a) are directly connected to one another, and such a composite material (10) .

FIG. 1



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Description

Technical Field

[0001] The present invention relates to a method for producing a composite material in which carbon nanotubes (hereinbelow, the carbon nanotubes are referred to as CNTs) are attached to the surface of a plurality of continuous carbon fiber constituting a carbon fiber bundle, and a composite material.

Background Art

[0002] Fiber-reinforced molded articles including reinforcing fibers dispersed in a resin, the base material, have excellent mechanical properties and dimensional stability, and thus find applications in a wide range of fields. CNT/carbon fiber composite materials having structures in which a plurality of CNTs is entangled to form a CNT network thin film on the surface of carbon fibers have been proposed as reinforcing fibers (for example, Patent Literature 1).

[0003] Carbon fiber bundles, formed by bundling continuous carbon fibers into each unit of thousands to tens of thousands, have excellent properties such as low density, high specific strength, and a high specific modulus of elasticity. Prepregs, obtained by impregnating such carbon fiber bundles with a resin, have promise for applications having stricter requirements on the performance (such as aeronautical and aerospace applications).

Citation List

Patent Literature

[0004] Patent Literature Japanese Patent Laid-Open No. 2013-76198

Summary of Invention

Technical Problem

[0005] In Patent Literature 1, a CNT network is formed on a carbon fiber surface by immersing carbon fibers in a dispersion containing CNTs and imparting energies such as vibrations, light irradiations, and thermal to the dispersion. It is mentioned that a fiber-reinforced molded article that takes advantage of the characteristics of a base material as well as includes the base material and carbon fibers strongly bonded to each other can be provided when the base material is impregnated with the composite material of Patent Literature 1.

[0006] In a carbon fiber bundle including a plurality of continuous carbon fibers, in the case in which CNTs are attached to the surface of each of the carbon fibers, more excellent reinforcing fibers also having CNT-derived properties (composite material) can be obtained. Such composite materials are required for producing high-strength prepregs.

[0007] It is thus an object of the present invention to provide a method for producing a composite material from which a high-strength prepreg having CNT-derived properties fully exerted is obtained and such a composite material.

Solution to Problem

[0008] The method for producing a composite material according to the present invention is characterized by comprising a step of immersing a carbon fiber bundle including a plurality of continuous carbon fibers in a carbon-nanotubes-isolated dispersion containing a plurality of isolatedly-dispersed carbon nanotubes and applying ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less to form a structure comprising a plurality of carbon nanotubes on a surface of each of the plurality of carbon fibers, wherein the structure is directly attached to the surface of each of the plurality of carbon fibers and has a network structure in which the carbon nanotubes are directly connected to one another.

[0009] The composite material according to the present invention is characterized by having been produced by the method aforementioned.

Advantageous Effect of Invention

[0010] According to the method for producing a composite material of the present invention, by immersing a carbon fiber bundle including a plurality of continuous carbon fibers in a CNT-isolated dispersion and applying ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less to the dispersion, CNTs are allowed to be attached to the surface of each carbon fibers in the carbon fiber bundle. Since the frequency exceeds 40 kHz, a possibility that the linearity of the carbon fibers in the carbon fiber bundle is disturbed is reduced. In the composite material to be obtained, there is substantially no entanglement among carbon fibers. Each carbon fiber in the carbon fiber bundle can contribute to the strength, and the strength inherent in the carbon fiber bundle is exerted. Furthermore, since the frequency is specified to be 180 kHz or less, CNTs can be allowed to be satisfactorily attached to the surface of each carbon fiber. In this manner, there is obtained a composite material that may sufficiently exert CNT-derived properties.

[0011] In the production method of the present invention, the carbon fiber bundle is immersed in a CNT-isolated dispersion in which CNTs are isolated dispersed. In the CNT-isolated dispersion, CNTs are dispersed in a state in which the CNTs are each physically separated and not entangled with one another in a dispersion medium. That such a CNT-isolated dispersion is used is one of the reasons why CNTs can be satisfactorily attached to the surface of each carbon fiber.

[0012] Since the composite material of the present invention is produced by the method of the present inven-

tion, there is substantially no entanglement of carbon fibers with one another, and the CNTs are satisfactorily attached to the surface of each of the carbon fibers. For this reason, it is possible to obtain a high-strength prepreg by impregnating the composite material of the present invention with a resin.

Brief Description of Drawings

[0013]

FIG. 1 is a partial schematic view illustrating the configuration of the composite material according to the present embodiment.

FIG. 2 is a schematic diagram showing the relation between the frequency of ultrasonic vibrations applied to a dispersion and the cavitation occurring in the dispersion.

FIG. 3 is an SEM micrograph of the composite material of Example 1, in which FIG. 3A shows a portion of the surface of a carbon fiber in a carbon fiber bundle and FIG. 3B is an enlarged photo of the carbon fiber surface.

FIG. 4 is an SEM micrograph of the composite material of Example 2, in which FIG. 4A shows a portion of the surface of a carbon fiber in a carbon fiber bundle and FIG. 4B is an enlarged photo of the carbon fiber surface.

FIG. 5 is an SEM micrograph of the composite material of Comparative Example 1, in which FIG. 5A shows a portion of the surface of a carbon fiber in a carbon fiber bundle and FIG. 5B is an enlarged photo of the carbon fiber surface.

FIG. 6 is an SEM micrograph of the composite material of Comparative Example 2, in which FIG. 6A shows a portion of the surface of a carbon fiber in a carbon fiber bundle and FIG. 6B is an enlarged photo of the carbon fiber surface.

FIG. 7 is an SEM micrograph of the composite material of Comparative Example 3, in which FIG. 7A shows a portion of the surface of a carbon fiber in a carbon fiber bundle and FIG. 7B is an enlarged photo of the carbon fiber surface.

FIG. 8 is a schematic view illustrating a carbon fiber to which CNTs are attached by a conventional method, in which FIG. 8A is a schematic view illustrating a state in which CNT aggregates are attached and FIG. 8B is a schematic view illustrating a state in which attachment is insufficient.

Description of Embodiment

[0014] The present inventors, with regard to producing a composite material by forming a structure containing CNTs on the surface of each carbon fiber, have established an approach to attach CNTs to the surface of carbon fibers by immersing the carbon fibers in a CNT dispersion and applying ultrasonics. Using this approach enables to form a structure in which a plurality of CNTs is directly connected to one another to form a network structure as well as are directly attached to the carbon fiber surface. Then, when this approach was applied to a carbon fiber bundle including a plurality of continuous carbon fibers to attach CNTs to the surface of the carbon fibers, entanglement of the carbon fiber with one another was observed. When entanglement of the carbon fibers with one another in the carbon fiber bundle is caused, the number of carbon fibers capable of contributing to the strength becomes lesser than the original number, and thus, the strength inherent in the carbon fiber bundle is not exerted. Even with a carbon fiber bundle that comprises carbon fibers having CNTs attached to their surface, it is difficult to obtain a high-strength prepreg by impregnating the bundle with a resin when entanglement of the carbon fibers with one another is caused.

[0015] Entanglement of the carbon fibers with one another in the carbon fiber bundle is responsible for disturbance in the linearity of the carbon fibers due to cavitation occurred in the dispersion by application of ultrasonics. The present inventors, with attention paid on this point, have enabled CNTs to attach to the surface of each of the carbon fibers while entanglement of the carbon fibers with one another in the carbon fiber bundle is avoided.

[0016] Hereinbelow, embodiments of the present invention will be described in detail with reference to the drawings.

1. Entire configuration

[0017] As shown in FIG. 1, a composite material 10 of the present embodiment comprises a carbon fiber bundle 12 that includes a plurality of continuous carbon fibers 12a. In the figure, only 10 carbon fibers 12a are illustrated for description, but the carbon fiber bundle 12 in the present embodiment is constituted by 10,000 to 30,000 carbon fibers 12a. The carbon fibers 12a constituting the carbon fiber bundle 12 align in one direction while maintaining the linearity substantially without entangling with one another.

[0018] The entanglement of the carbon fibers 12a in the carbon fiber bundle 12 can be evaluated with respect to the degree of disturbance of the carbon fibers 12a. For example, the carbon fiber bundle 12 is observed by means of a scanning electron microscope (SEM) at a constant magnification to determine the length of a predetermined number (for example, 10) of the carbon fibers 12a. The degree of disturbance of the carbon fibers 12a can be evaluated based on variations in the length, the difference between the maximum value and the minimum value, and the standard deviation for the predetermined number of the carbon fibers 12a. That the carbon fibers 12a are not substantially entangled also can be determined by measuring the degree of entanglement, for example, in accordance with the degree of intermingle measurement method of JIS L1013: 2010 "Testing methods for man-made fiber filament yarns". The smaller the

degree of intermingle measured, the lesser the entanglement of the carbon fibers 12a with one another in the carbon fiber bundle 12. Accordingly, when a prepreg is produced, the carbon fibers 12a are homogeneously spread with ease, and each of the carbon fibers 12a can contribute to the strength. On the surface of each of such carbon fibers 12a, a structure 14 is formed.

[0019] The carbon fibers 12a are fibers having a diameter of about 5 to 20 μm, obtained by baking organic fibers derived from petroleum, coal, or coal tar such as polyacrylonitrile, rayon, and pitch or organic fibers derived from wood or plant fibers.

[0020] The structure 14 on the surface of each of the carbon fibers 12a includes a plurality of CNTs 14a. The CNTs 14a are homogeneously dispersed and entangled across substantially the entire surface of the carbon fibers 12a, being in direct contact with or directly connected to one another to form a network structure. Among each of the CNTs 14a, there is preferably no intervening material, for example, a dispersing agent such as a surfactant and an adhesive. Additionally, CNTs 14a are directly attached to the surface of the carbon fibers 12a. Connection as referred to herein includes physical connection (mere contact). Attachment as referred to herein refers to bonding due to a van der Waals force. Furthermore, "direct contact or direct connection" includes a state in which a plurality of CNTs is integrally connected in addition to a state in which a plurality of CNTs is merely in contact with one another, and should not be interpreted limitedly.

[0021] The length of the CNTs 14a forming the structure 14 is preferably 0.1 to 50 μm. When the length of the CNTs 14a is 0.1 μm or more, the CNTs 14a are entangled with one another to be directly connected. When the length of the CNTs 14a is 50 μm or less, the CNTs 14a become likely to be dispersed homogeneously. In contrast, when the length of the CNTs 14a is less than 0.1 μm, the CNTs 14a become difficult to entangle with one another. When the length of the CNTs 14a exceeds 50 μm, the CNTs 14a become likely to aggregate.

[0022] The CNTs 14a preferably have an average diameter of about 30 nm or less. When the diameter of the CNTs 14a is 30 nm or less, the CNTs 14a are highly flexible and can form a network structure on the surface of each of the carbon fibers 12a. In contrast, when the diameter of the CNTs 14a is more than 30 nm, the CNTs 14a lose flexibility and hardly form a network structure on the surface of the each of the carbon fibers 12a. Incidentally, the diameter of the CNTs 14a is an average diameter measured by using a transmission electron microscope (TEM) micrograph. The CNTs 14a preferably have an average diameter of about 20 nm or less.

[0023] A plurality of CNTs 14a are preferably attached homogeneously to the surface of each of the carbon fibers 12a in the carbon fiber bundle 12. The attachment state of the CNTs 14a on the surface of the carbon fibers 12a can be observed by means of an SEM and evaluated by visually inspecting the image obtained.

[0024] Incidentally, in the case in which the CNTs are allowed to attach to the carbon fibers by the conventional method, carbon fibers 32a that include CNT aggregates 34b, in addition to CNTs 34a, attached to their surface may exist in the carbon fiber bundle, as shown in FIG. 8A. Alternatively, as shown in FIG. 8B, carbon fibers 42a that have no structure formed on their surface because of an insufficient amount of CNTs 44a attached may be included in a carbon fiber bundle 42.

[0025] In contrast to this, in the present embodiment, carbon fibers that have CNT aggregates attached to their surface are not substantially included in the carbon fiber bundle. Carbon fibers that have no structure formed on their surface because of an insufficient amount of CNTs attached do not either exist in the carbon fiber bundle.

[0026] In the composite material 10 of the present embodiment, the CNTs 14a are directly attached to the surface of each of the carbon fibers 12a in the carbon fiber bundle 12. In other words, no dispersing agent such as a surfactant, an adhesive or the like intervene between the CNTs 14a and the surface of the carbon fibers, and the CNTs 14a are directly attached to the surface of the carbon fibers 12a.

2. Production Method

[0027] Next, the method for producing the composite material 10 according to the present embodiment will be described. The composite material 10 can be produced by immersing the carbon fiber bundle 12 including the plurality of continuous carbon fibers 12a in a CNT-isolated dispersion in which the CNTs 14a are isolatedly dispersed (hereinbelow, the CNT-isolated dispersion is also merely referred to as the dispersion) and applying ultrasonic vibrations at a predetermined frequency to the dispersion to form the structure 14 on the surface of each of the carbon fibers 12a. Hereinbelow, each step will be described in order.

(Preparation of Dispersion)

[0028] For preparation of the dispersion, the CNTs 14a produced as follows can be used. The CNTs 14a can be produced by depositing a catalytic film formed of aluminum or iron onto a silicon substrate by using the thermal CVD method as described in Japanese Patent Laid-Open No. 2007-126311, for example, microparticulating the catalytic metals for CNT growth, and bringing a hydrocarbon gas into contact with the catalytic metals in a heating atmosphere. CNTs obtained by other production methods such as arc discharge and laser evaporation also can be used, but those containing impurities other than CNTs as little as possible are preferably used. These impurities may be removed by high temperature annealing in an inert gas after CNTs are produced. CNTs produced in this production example are linearly-oriented long CNTs having a diameter of 30 nm or less and a length of several hundred micrometers to several millim-

eters, thus having a high aspect ratio. CNTs may be single-walled or multi-walled CNTs, and preferably multi-walled CNTs.

[0029] Subsequently, the CNTs 14a produced above are used to prepare a dispersion in which the CNTs 14a are isolatedly dispersed. Isolated dispersion refers to a state in which CNTs 14a are dispersed in a dispersion medium so that the CNTs 14a are each physically separated and not entangled with one another and means a state in which aggregates each formed by two or more CNTs 14a aggregated in a bundle form account for 10% or less of all the CNTs.

[0030] The dispersion is prepared by adding CNTs 14a produced as above to a dispersion medium, and a homogenizer, a shear disperser, an ultrasonic disperser or the like is used to achieve homogeneous dispersion of the CNTs 14a. Examples of the dispersion medium that can be used include water, alcohols such as ethanol, methanol, and isopropyl alcohol, organic solvents such as toluene, acetone, tetrahydrofuran (THF), methyl ethyl ketone (MEK), hexane, normal hexane, ethyl ether, xylene, methyl acetate, and ethyl acetate. Additives such as a dispersing agent and a surfactant are not necessarily required for preparing the dispersion, but such additives may be used within a range in which the functions of carbon fibers 12a and CNTs 14a are not limited.

(Formation of Structure)

[0031] Ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less are applied to the dispersion prepared as described above, in which the carbon fiber bundle 12 including a plurality of continuous carbon fibers 12a is immersed. Application of ultrasonic vibrations allows a plurality of CNTs 14a to be directly attached to the surface of each of the carbon fibers 12a in the carbon fiber bundle 12. The CNTs 14a attached to the surface of each of the carbon fibers 12a are directly connected to one another to form a network structure, forming a structure 14 on the surface of each of the carbon fibers 12a.

[0032] When the frequency is more than 40 kHz, entanglement of the carbon fibers 12a in the carbon fiber bundle 12 with one another is suppressed. When the frequency is 180 kHz or less, the CNTs 14a are satisfactorily attached to the surface of the carbon fibers 12a. In contrast when the frequency is 40 kHz or less, the entanglement of the carbon fibers 12a with one another becomes pronounced. When the frequency is more than 180 kHz, the attachment state of the CNTs 14a on the surface of the carbon fibers 12a becomes defective, and thus the structure 14 cannot be formed. In order to further reduce the entanglement of the carbon fibers 12a, the ultrasonic frequency is preferably 100 kHz or more, more preferably 130 kHz or more.

[0033] Application of ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less to the dispersion creates a reversible reaction state in which a dispersion state of the CNTs 14a and an aggregation state of the CNTs 14a are continuously occurred in the dispersion.

[0034] In the dispersion in this reversible reaction state, the carbon fiber bundle 12 including the plurality of continuous carbon fibers 12a is immersed. This causes a reversible reaction state including a dispersion state and an aggregation state of the CNTs 14a also on the surface of each of the carbon fibers 12a. On transfer from the dispersion state to the aggregation state, CNTs 14a are attached to the surface of each of the carbon fibers 12a.

[0035] When aggregating, CNTs 14a are under the action of a van der Waals force, which attaches the CNTs 14a to the surface of the carbon fibers 12a. Thereafter, the carbon fiber bundle 12 is withdrawn from the dispersion and dried, and thus, the composite material 10 in which a network structure is formed on the surface of each of the carbon fibers 12a in the carbon fiber bundle 12 can be obtained. Drying can be achieved by placing the bundle 12 on a hot plate, for example.

[0036] The composite material 10 of the present embodiment can be formed into a prepreg by opening the carbon fibers 12a in the carbon fiber bundle 12 and impregnating the opened fibers with a resin. Examples of the resin for impregnation include, but not particularly limited to, thermosetting resins such as epoxy resin and thermoplastic resins such as phenoxy resin and nylon.

[0037] As described above, substantially no entanglement of the carbon fibers 12a with one another in the carbon fiber bundle 12 exists in the composite material 10 of the present embodiment. Thus, the plurality of carbon fibers 12a is homogeneously spread with ease when a prepreg is produced. Furthermore, a structure 14 to which the CNTs 14a are satisfactorily attached is formed on the surface of each of the carbon fibers 12a in the carbon fiber bundle 12. In a prepreg, obtained by impregnating the composite material 10 like this with a resin, the possibility of reduction in the strength caused by the entanglement of the carbon fibers 12a with one another is extremely low. Since the CNTs 14a are satisfactorily attached to the surface of each of the carbon fibers 12a and form the structure 14, the prepreg to be obtained can sufficiently exert its CNT-derived properties.

3. Action and Effects

[0038] In the method for producing a composite material according to the present embodiment, a carbon fiber bundle including a plurality of continuous carbon fibers is immersed in a CNT-isolated dispersion, and ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less are applied to the dispersion. The present inventors have found that a frequency range of more than 40 kHz and 180 kHz or less is optimal in the manner described below.

[0039] As shown in FIG. 2, the lower the frequency of the ultrasonic vibrations to be applied on the dispersion, the higher the occurrence frequency of cavitation that

occurs in the dispersion. In contrast, the higher the frequency, the lower the occurrence frequency of cavitation.

[0040] When the frequency of ultrasonic vibrations is low, the dispersibility of the CNTs 14a in the dispersion is also increased by the effect of the cavitation occurred. When the carbon fiber bundle 12 including the plurality of continuous carbon fibers 12a is immersed in a dispersion in which cavitation is active, the CNTs 14a in the dispersion are satisfactorily attached to the surface of each of the carbon fibers 12a. Cavitation is advantageous in respect of facilitating satisfactory attachment of the CNTs 14a to the surface of the carbon fibers 12a. However, cavitation disturbs, due to its large mechanical vibrations, the linearity of the carbon fibers 12a in the carbon fiber bundle 12. Due to disturbance in the linearity of the carbon fibers 12a, entanglement of the carbon fibers 12a with one another is caused.

[0041] In contrast, when the ultrasonic frequency is increased, the occurrence frequency of cavitation is reduced, and thus disturbance in the linearity of the carbon fibers 12a in the carbon fiber 12 is suppressed. Accordingly, entanglement of the carbon fibers 12a with one another is scarce. However, in this case, since the occurrence frequency of cavitation in the dispersion is reduced, the attachment state of the CNTs 14a on the surface of the carbon fibers 12a also tends to be reduced.

[0042] As a result of intensive studies, the present inventors have obtained the following findings. In other words, a shock wave ascribed to cavitation occurs in the dispersion and entanglement of the carbon fibers 12a is caused by large mechanical vibrations in the case in which the frequency of ultrasonic vibrations is 40 kHz or less. The attachment state of CNTs 14a to the surface of each of the carbon fibers 12a becomes defective in the case in which the frequency is more than 180 kHz. With a frequency of 180 kHz or less, even if cavitation has not occurred, only the effect of the ultrasonic vibrations enables CNTs 14a to be satisfactorily attached to the surface of the carbon fibers 12a.

[0043] In the present embodiment, setting the frequency of ultrasonic vibrations to be applied to the dispersion in which the carbon fiber bundle 12 is immersed to more than 40 kHz and 180 kHz or less has enabled the CNTs 14a to be satisfactorily attached to the surface of each of the carbon fibers 12a while disturbance in the linearity in the carbon fibers 12a was suppressed to reduce entanglement of the carbon fibers 12a with one another.

[0044] Furthermore, in the present embodiment, the carbon fiber bundle 12 is immersed in a CNT-isolated dispersion in which the CNTs 14a are isolatedly dispersed. In the CNT-isolated dispersion, the CNTs 14a are dispersed in a state in which the CNTs 14a are each physically separated and not entangled with one another in a dispersion medium. Use of such a dispersion also leads to satisfactory attachment of CNTs to the surface of each of the carbon fibers 12a in the carbon fiber bundle 12.

4. Modified Example

[0045] The present invention is not limited to the embodiment described above and can be varied within the spirit of the present invention as appropriate.

[0046] As the carbon fiber bundle 12, a so-called regular tow constituted by 10,000 to 30,000 carbon fibers 12a can be used. The diameter of the carbon fibers 12a can be set within a range of 5 to 10 μm as appropriate.

[0047] When the carbon fiber 12a is dried to obtain the structure 14 on the surface, the dispersion medium may be evaporated from the carbon fiber bundle 12 by placing the bundle on a hot plate, or otherwise by using an evaporator.

5. Example

[0048] Hereinbelow, the present invention will be described in detail with reference to examples, but the present invention is not intended to be limited only to the following examples.

[0049] A composite material of Example 1 was produced in the procedure described in the production method described above. CNTs 14a used were Multi-walled Carbon Nanotubes (MW-CNTs) which were grown to have a diameter of 10 to 15 nm and a length of 100 μm or more on a silicon substrate by the thermal CVD method. For removal of catalyst residues from the CNTs 14a, a 3:1 mixed acid of sulfuric acid and nitric acid was used, and after washing, the CNTs 14a were filtered and dried. To cut the CNTs 14a, the CNTs 14a were ground in a dispersion medium by an ultrasonic homogenizer to a length of 0.5 to 10 μm. Methyl ethyl ketone was used as the CNT dispersion medium to prepare a dispersion. The concentration of the CNTs 14a in the dispersion was set to 0.01 wt%. This dispersion contains no dispersing agent and adhesive.

[0050] Then, while ultrasonic vibrations at 130 kHz was applied to the dispersion, T700SC-12000 (manufactured by Toray Industries, Inc.) as a carbon fiber bundle 12 was placed in the dispersion. The carbon fiber bundle 12 used herein include 12,000 carbon fibers 12a. The carbon fibers 12a each have a diameter of about 7 μm and a length of about 100 m. The carbon fiber bundle 12 was maintained in the dispersion for 10 seconds.

[0051] Thereafter, the carbon fiber bundle 12 was removed from the dispersion and dried on a hot plate at about 80°C to form a structure 14 on the surface of each of the carbon fibers 12a constituting the carbon fiber bundle 12. In this manner, the composite material 10 of Example 1 was obtained.

[0052] Additionally, the composite material of Example 2 was produced in the same manner as Example 1 except that the ultrasonic frequency was changed to 160 kHz. Furthermore, the composite materials of Comparative Examples 1, 2, and 3 were produced in the same manner as Example 1 except that the ultrasonic frequency was changed to 28 kHz, 38 kHz, and 200 kHz, respectively.

[0053] The surface of the carbon fibers in the composite materials of Examples 1 and 2 and Comparative Examples 1 to 3 was observed by an SEM, and the images obtained are shown in FIGs. 3A and 3B to 7A and 7B.

[0054] FIG. 3A is an SEM micrograph showing a portion of the surface of the carbon fibers 12a in the carbon fiber bundle 12 in the composite material of Example 1, and FIG. 3B is an enlarged photo of FIG. 3A. A state in which a plurality of CNTs 14a are dispersed homogeneously on and attached to the surface of the carbon fibers 12a by forming a structure 14 is shown.

[0055] FIG. 4A is an SEM micrograph showing a portion of the surface of the carbon fibers 12a in the carbon fiber bundle 12 in the composite material of Example 2, and FIG. 4B is an enlarged photo of FIG. 4A. Similarly to Example 1, it can be seen that the plurality of CNTs 14a are dispersed homogeneously on and attached to the surface of the carbon fibers 12a by forming a structure 14 also in Example 2.

[0056] In the carbon fibers 12a of the composite materials of Example 1 and Example 2, it was confirmed that substantially no entanglement of the carbon fibers 12a exists in the carbon fiber bundle 12.

[0057] With regard to producing the composite materials, the frequency of ultrasonic vibrations was 130 kHz in Example 1 and 160 kHz in Example 2. In the composite materials of Examples 1 and 2, the CNTs 14a are satisfactorily attached to the surface of each of the carbon fibers 12a in the carbon fiber bundle 12 and form the structure 14 on the surface. Furthermore, substantially no entanglement of the carbon fibers 12a with one another exists in the carbon fiber bundle 12. It is assumed that prepregs obtained by impregnating such composite materials of Example 1 and Example 2 with a resin are capable of sufficiently exerting CNT-derived properties and have high strength.

[0058] FIG. 5A is an SEM micrograph showing a portion of the surface of carbon fibers 52a in the carbon fiber bundle in the composite material of Comparative Example 1, and FIG. 5B is an enlarged photo of FIG. 5A. FIG. 6A is an SEM micrograph showing a portion of the surface of the carbon fibers 52a in the carbon fiber bundle in the composite material of Comparative Example 2, and FIG. 6B is an enlarged photo of FIG. 6A. FIG. 5B and FIG. 6B shows that a plurality of CNTs 14a are dispersed to form the structure 14 on the surface of the carbon fibers 52a in the composite materials of Comparative Examples 1 and 2.

[0059] In the composite materials of Comparative Examples 1 and 2, much entanglement of the carbon fibers 52a with one another in the carbon fiber bundle has occurred. With regard to producing the composite materials, the frequency of ultrasonic vibrations was 28 kHz in Comparative Example 1 and 38 kHz in Comparative Example 2. Since entanglement of the carbon fibers 52a with one another in the carbon fiber bundle has been occurred, it is difficult to provide high-strength prepregs even if the composite materials of Comparative Examples 1 and 2 are impregnated with a resin.

[0060] FIG. 7A is an SEM micrograph showing a portion of the surface of the carbon fibers 62a in the carbon fiber bundle in the composite material of Comparative Example 3, and FIG. 7B is an enlarged photo of FIG. 7A. As shown in FIG. 7B, carbon fibers 62a that have few CNTs 14a attached to their surface are included in the composite material of Comparative Example 3. On the surface of these carbon fibers 62a, no structure 14 is formed. In Comparative Example 3, the frequency of ultrasonic vibrations was set to 200 kHz with regard to producing the composite materials. Since no structure 14 constituted by a network structure of a plurality of CNTs 14a has been formed on the surface of the carbon fibers 62a, a prepreg in which CNT-derived properties are sufficiently exerted is not obtained even if the composite material of Comparative Examples 3 is impregnated with a resin.

[0061] Provided that a dispersion in which CNTs are isolatedly dispersed is used and ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less are applied, conditions other than these are not particularly limited and can be varied as appropriate. The carbon fiber bundle including a plurality of continuous carbon fiber can be used to produce a composite material from which a high-strength prepreg having CNT-derived properties fully exerted is obtained.

Reference Signs List

[0062]

10 Composite material
12, 42 Carbon fiber bundle
12a, 32a, 42a, 52a, 62a Carbon fiber
34b CNT aggregate
14 Structure
14a, 34a, 44a Carbon nanotube (CNT)

Claims

1. A method for producing a composite material, comprising
a step of immersing a carbon fiber bundle including a plurality of continuous carbon fibers in a carbon-nanotubes-isolated dispersion containing a plurality of isolatedly-dispersed carbon nanotubes and applying ultrasonic vibrations at a frequency of more than 40 kHz and 180 kHz or less to form a structure comprising a plurality of carbon nanotubes on a surface of each of the plurality of carbon fibers,
wherein the structure is directly attached to the surface of each of the plurality of carbon fibers and has a network structure in which the carbon nanotubes are directly connected to one another.

2. The method for producing a composite material ac-

cording to claim 1, wherein the carbon fiber bundle comprises 10,000 to 30,000 carbon fibers.

3. The method for producing a composite material according to claim 1 or 2, wherein the frequency of the ultrasonic vibrations is 100 kHz or more.

4. A composite material produced by the method according to any one of claims 1 to 3.

FIG. 1

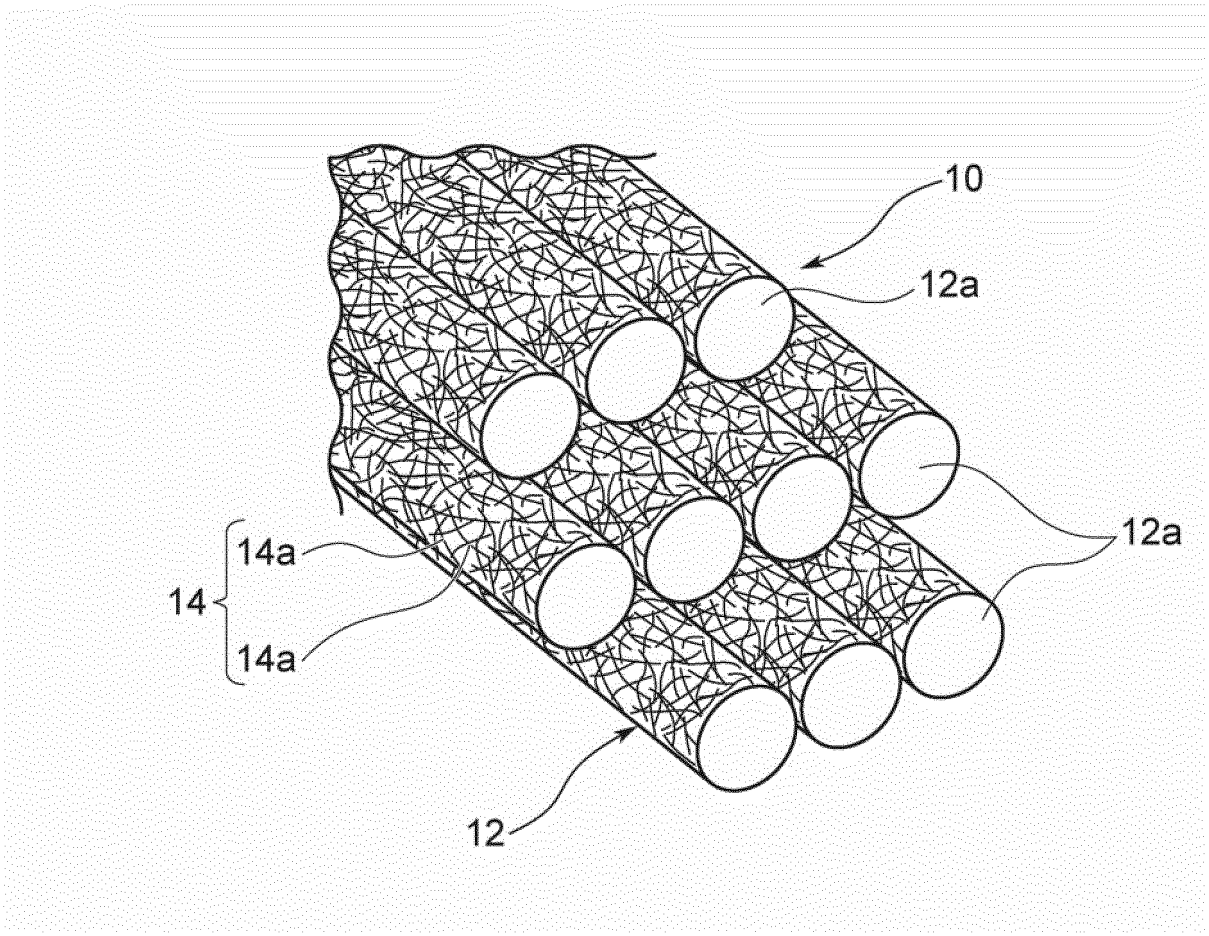

10
12a
12a
14
14a
14a
12

FIG. 2

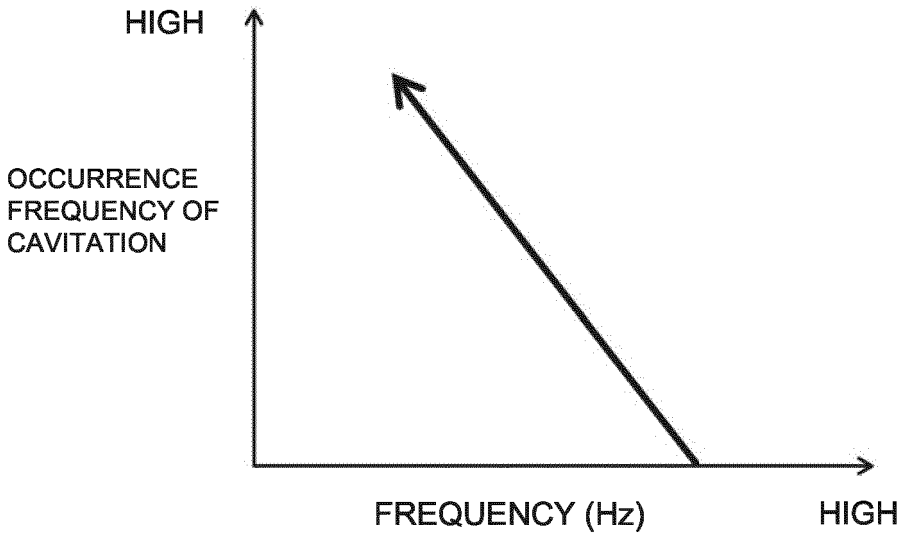

HIGH
OCCURRENCE FREQUENCY OF CAVITATION
FREQUENCY (Hz)
HIGH

FIG. 3A

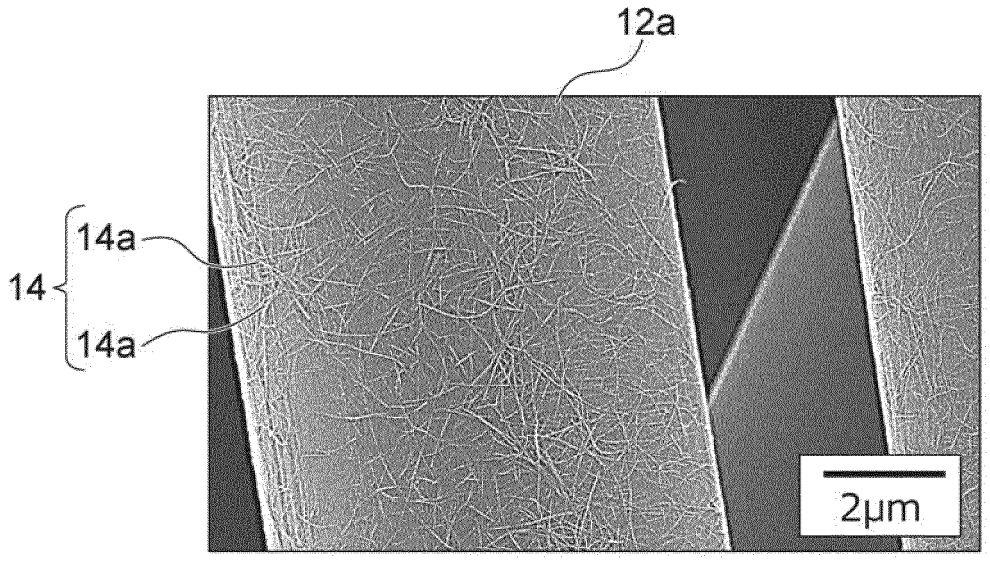


FIG. 3B

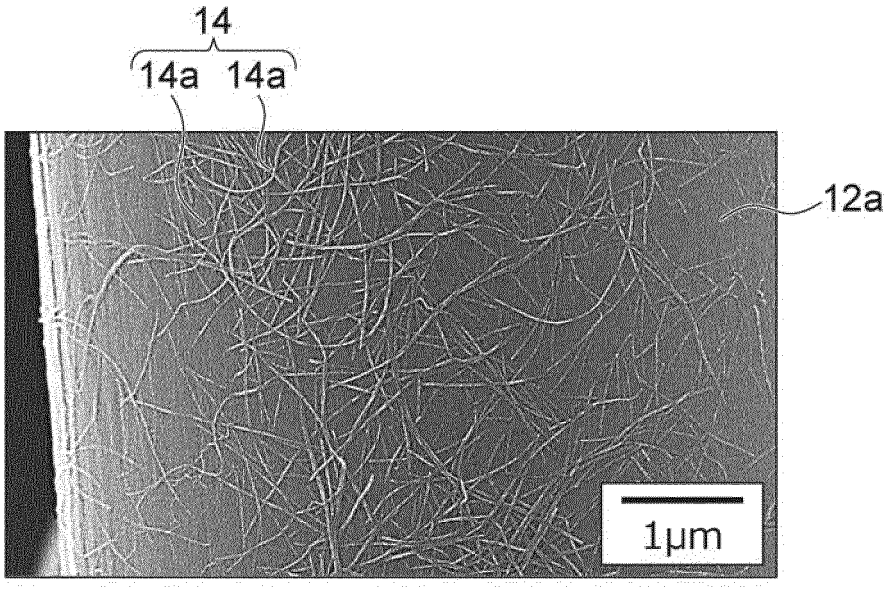


FIG. 4A

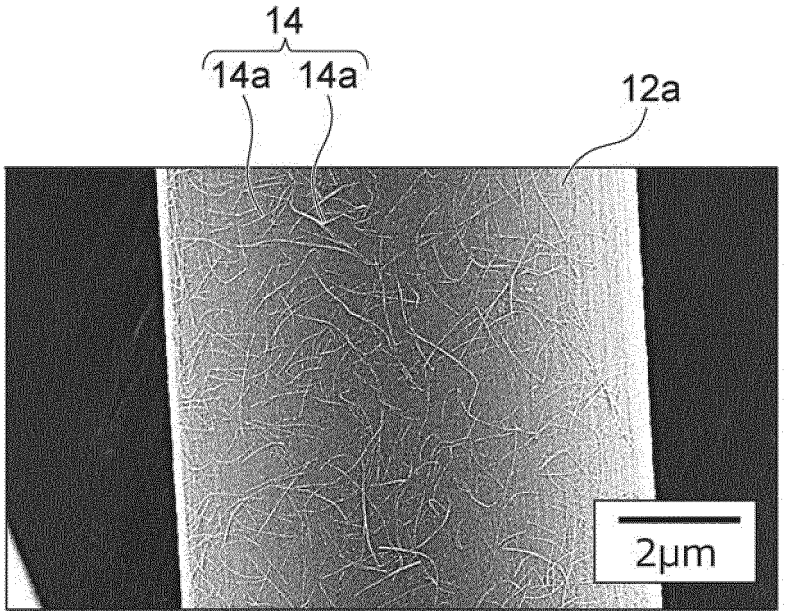


FIG. 4B

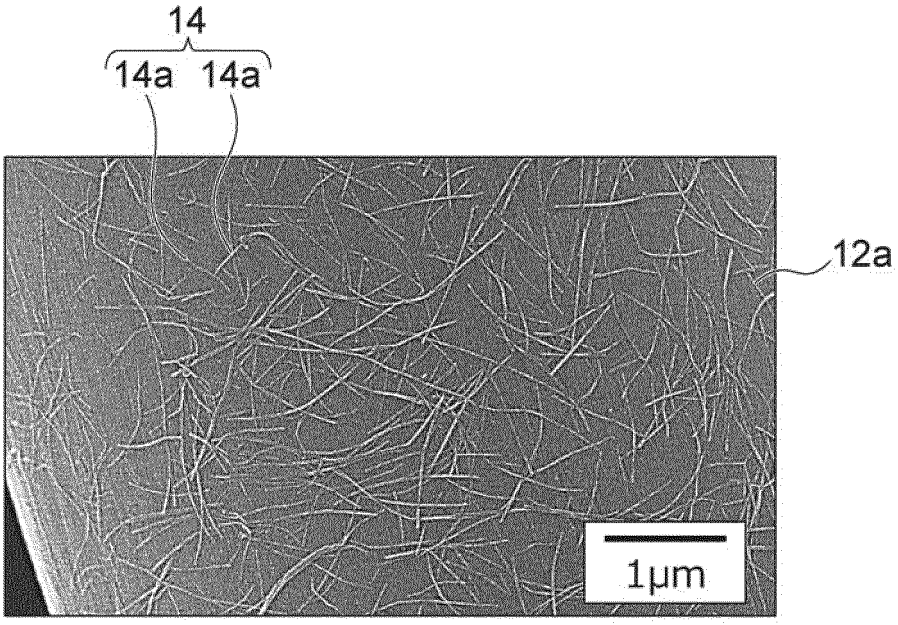


FIG. 5A

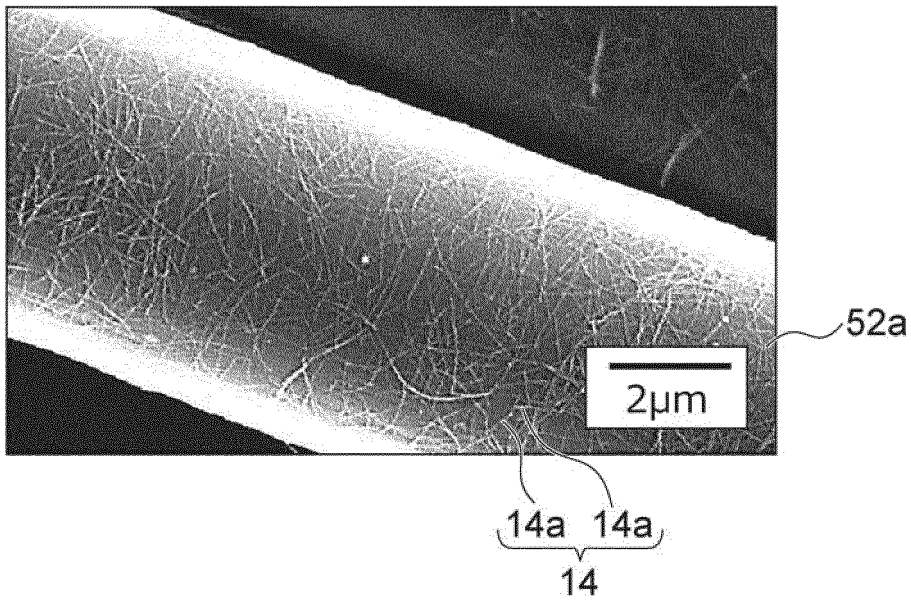


FIG. 5B

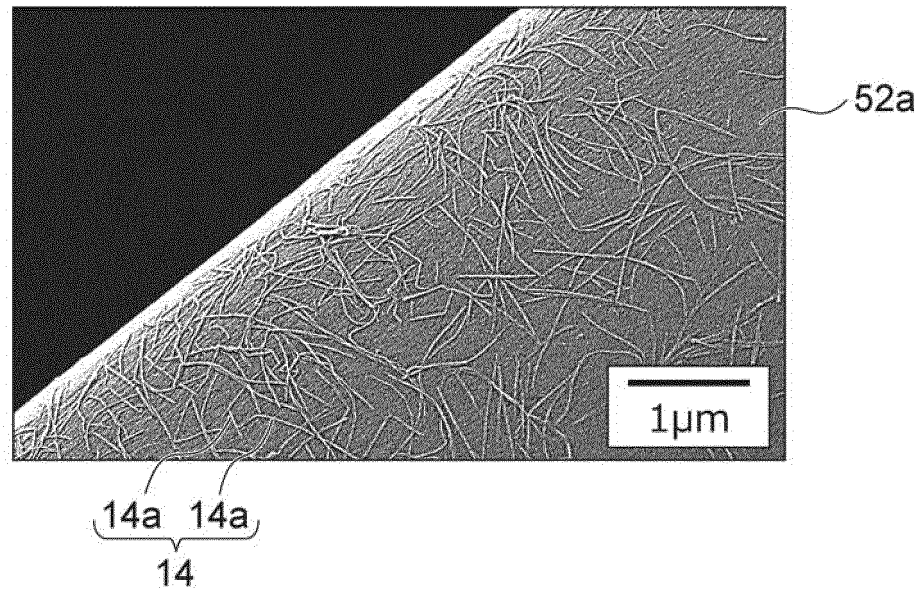


FIG. 6A

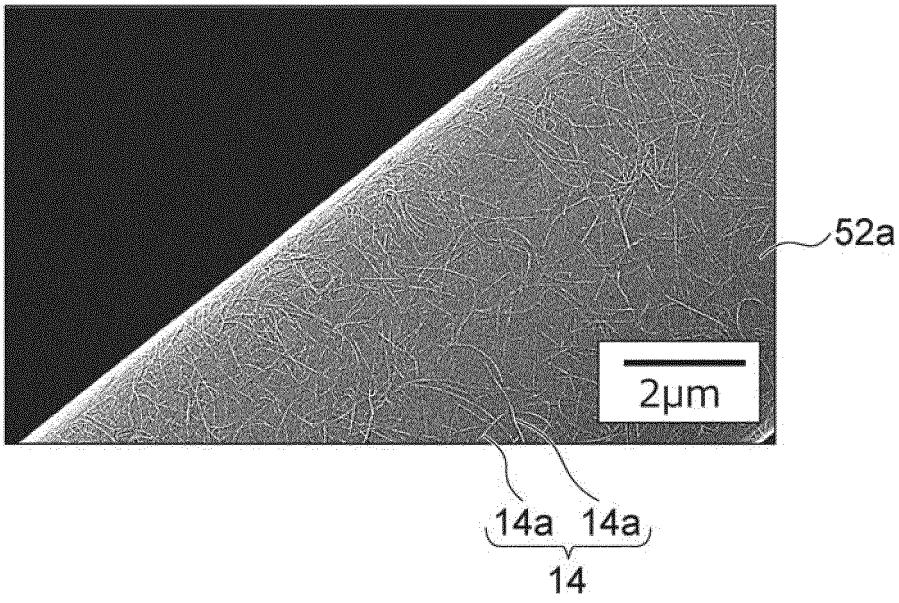


FIG. 6B

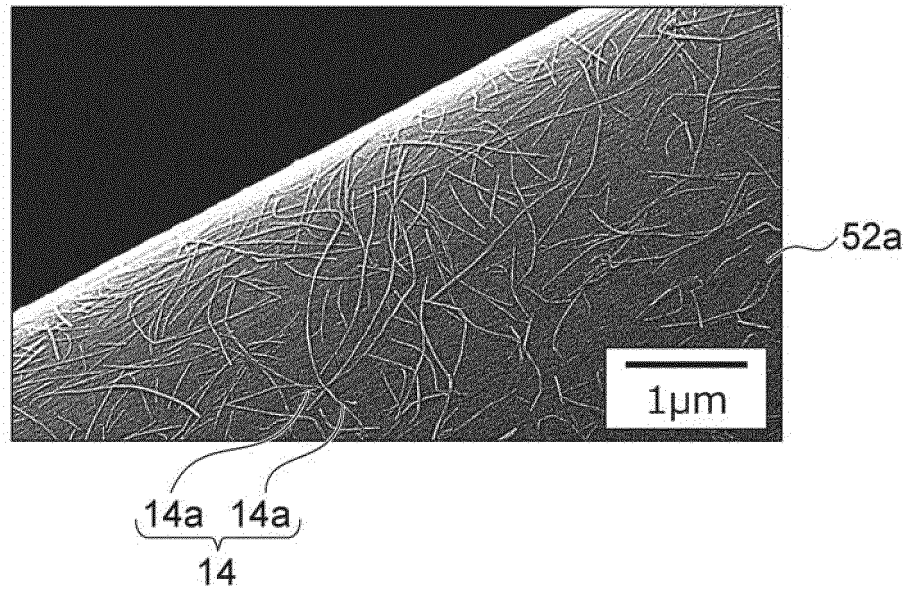


FIG. 7A

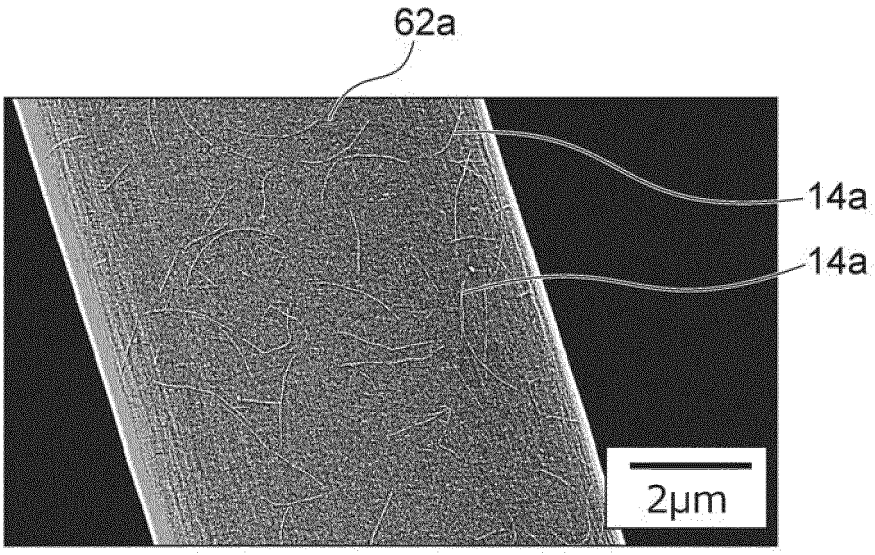


FIG. 7B

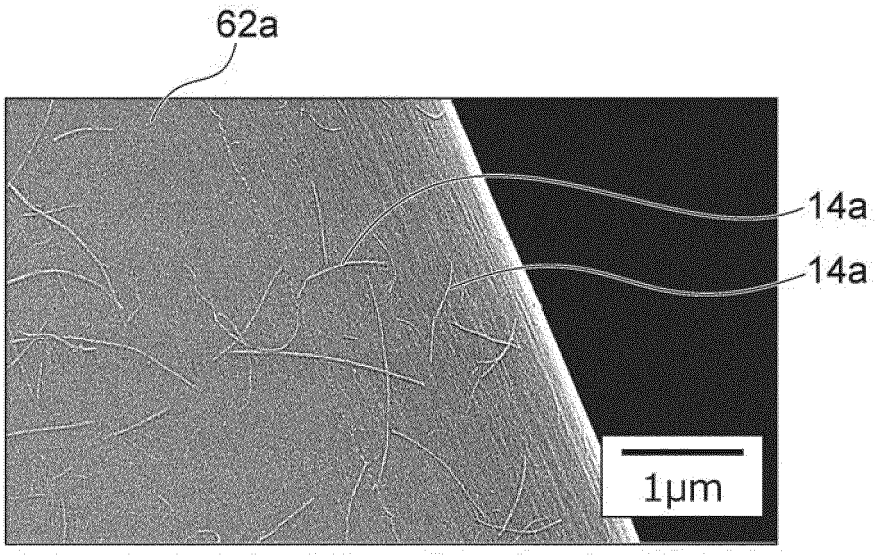


FIG. 8A

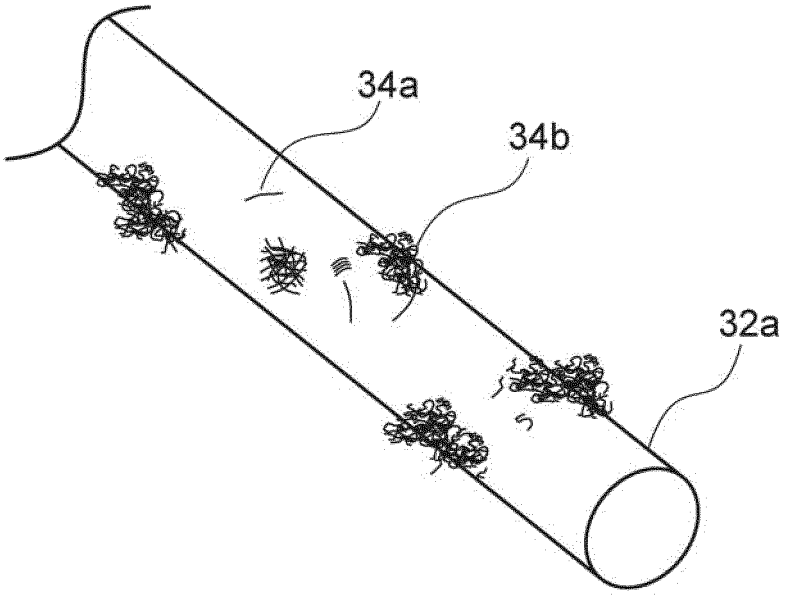
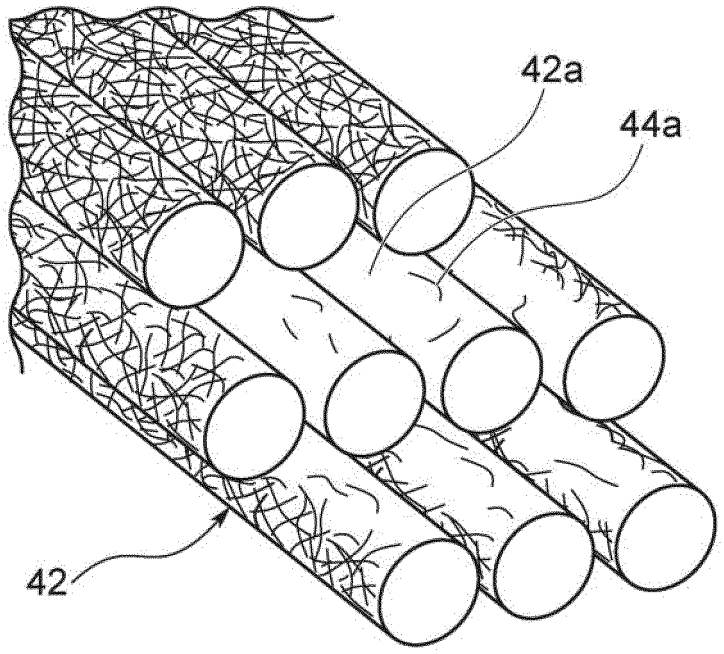


FIG. 8B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/060464

A. CLASSIFICATION OF SUBJECT MATTER
D06M11/74(2006.01)i, *D06M10/02*(2006.01)i, *D06M101/40*(2006.01)n

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)
D06M10/00-11/84, D06M16/00, D06M19/00-23/18, C01B31/00-31/14,
D01F9/08-9/32, B29B11/16, B29B15/08-15/14, C08J5/04-5/10, C08J5/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016
Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 2014/175319 A1 (Nitta Corp.), 30 October 2014 (30.10.2014), claims; paragraphs [0046] to [0049] & EP 2990380 A1 claims; paragraphs [0047] to [0050] & US 2016/0083899 A1 & TW 201518571 A & CN 105121339 A & KR 10-2016-0002785 A	4 1-3
X A	JP 2013-76198 A (Nitta Corp.), 25 April 2013 (25.04.2013), claims; paragraphs [0030], [0031]; fig. 1 (Family: none)	4 1-3

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

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 June 2016 (08.06.16)	21 June 2016 (21.06.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

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Patent documents cited in the description

- JP 2007126311 A **[0028]**