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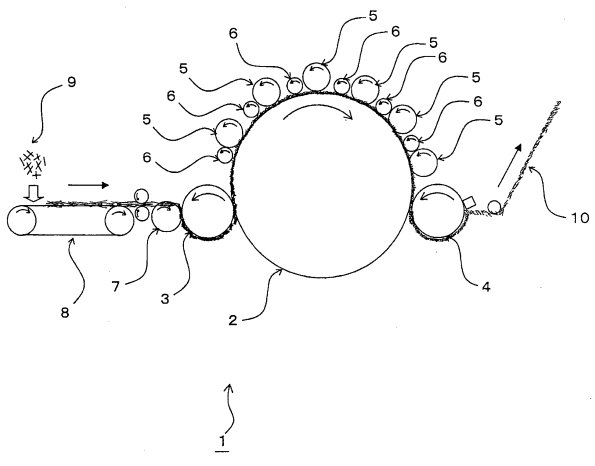
(54) **CARBON FIBER NONWOVEN**

(57) A carbon fiber nonwoven fabric in which carbon fibers are sized with an aliphatic compound having a plurality of epoxy groups or a specific aromatic compound; the number average x of carbon fibers forming a carbon fiber bundle (1), in which the number of carbon fibers forming the carbon fiber bundle is 90 or more, is in the range of 90 to 1,000 fibers per bundle among the carbon fiber bundles in the carbon fiber nonwoven fabric; and the standard deviation σ of the number of carbon fibers forming the carbon fiber bundle (1) is in the range of 50 to 500. It is possible to provide a carbon fiber nonwoven fabric in which high flowability and mechanical properties can be both satisfied with small variability in mechanical properties when a carbon fiber composite material is molded, and which also has an excellent shaping property for a carbon fiber mat.

FIG. 1



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Description

Technical Field of the Invention

[0001] The present invention relates to a carbon fiber nonwoven fabric, and specifically, to a carbon fiber nonwoven fabric which can satisfy both of high flowability and mechanical properties when a molded article of a carbon fiber composite material is made using the same.

Background Art of the Invention

[0002] A carbon fiber composite material comprising carbon fibers and a thermoplastic resin is used for manufacture of various molded articles, and various technologies, aiming high mechanical properties of a manufactured molded article and a good flowability at the time of the manufacture, have been proposed. Among those, by forming carbon fibers in the carbon fiber composite material as a formation of a nonwoven fabric, for example, in Patent document 1, a carbon fiber nonwoven fabric is proposed wherein the proportion of specified carbon fiber bundles in a carbon fiber nonwoven fabric relative to the whole amount of fibers is suppressed to be low, and the average number of fibers in the respective specified carbon fiber bundles is controlled in a specified range.

[0003] However, in such a carbon fiber nonwoven fabric as described in Patent document 1 wherein the carbon fiber bundles in the carbon fiber nonwoven fabric are thin, the proportion of the bundles is few and the carbon fibers are spread, although the mechanical properties of a molded article of a carbon fiber composite material manufactured using the same are excellent, the flowability at the time of molding is low and the moldability is poor. This is because the carbon fibers, which are reinforcing fibers, are sufficiently distributed, therefore a stress is hard to be concentrated and the reinforcing effect due to the carbon fibers is sufficiently exhibited, on the other hand, the carbon fibers are crossed to each other to restrict their movements and therefore the carbon fibers become hard to be moved.

[0004] On the other hand, in Patent document 2, a composite material is proposed wherein the proportion of specified carbon fiber bundles in a carbon fiber nonwoven fabric relative to the whole amount of fibers, similar to that described above, is set higher, and the average number of fibers in the respective specified carbon fiber bundles is controlled in another specified range. However, in such a carbon fiber nonwoven fabric as described in Patent document 2 wherein the carbon fiber bundles are thick and the proportion of the bundles is many, although the flowability at the time of manufacturing a molded article of a carbon fiber composite material using the same is high and the moldability is excellent, the mechanical properties are low and the variations in the mechanical properties are great. This is because the impregnation property of a resin into the carbon fiber bundles because the bundles are thick, and a stress is liable to be concentrated to end portions of the carbon fibers, but the carbon fibers are easily moved because the carbon fibers do not form networks.

Prior art documents

Patent documents

[0005]

Patent document 1: JP-A-2012-158846
Patent document 2: JP-A-2012-158847

Summary of the Invention

Problems to be solved by the Invention

[0006] Accordingly, an object of the present invention is to provide a carbon fiber nonwoven fabric in which high flowability and mechanical properties can be both satisfied with small variability in mechanical properties when a carbon fiber composite material is molded, and which also has an excellent shaping property for a carbon fiber mat.

Means for solving the Problems

[0007] To achieve the above-described object, a carbon fiber nonwoven fabric according to the present invention has the following structures.

(1) A carbon fiber nonwoven fabric including carbon fibers, characterized in that the carbon fibers are sized with an

aliphatic compound having a plurality of epoxy groups, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000 fibers per bundle among carbon fiber bundles in the carbon fiber nonwoven fabric, and a standard deviation σ of the number of carbon fibers forming the carbon fiber bundle (1) is in a range of 50 to 500.

(2) A carbon fiber nonwoven fabric including carbon fibers, characterized in that the carbon fibers are sized with an aromatic compound having a plurality of epoxy groups in which a number of atoms present between an epoxy group and an aromatic ring is 6 or more, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000 fibers per bundle among carbon fiber bundles in the carbon fiber nonwoven fabric, and a standard deviation σ of the number of carbon fibers forming the carbon fiber bundle (1) is in a range of 50 to 500.

(3) The carbon fiber nonwoven fabric according to (1) or (2), wherein the compound having a plurality of epoxy groups is a compound having an epoxy group at each end of the longest atomic chain.

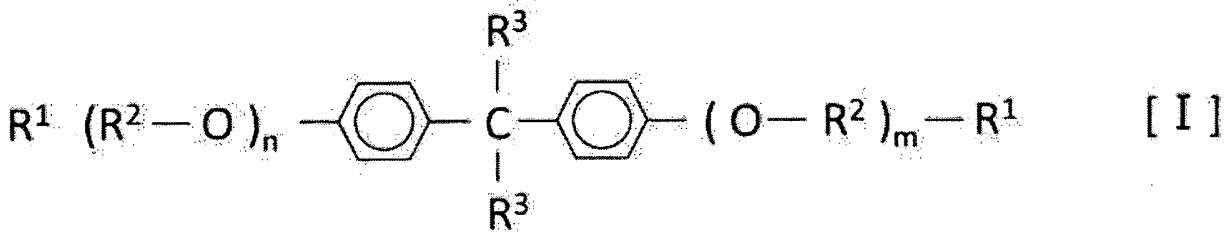
(4) The carbon fiber nonwoven fabric according to (3), wherein the compound having a plurality of epoxy groups is a compound having an epoxy group only at each end of the longest atomic chain.

(5) The carbon fiber nonwoven fabric according to (1) or (3), wherein a number of atoms of the longest atomic chain of the aliphatic compound having a plurality of epoxy groups is in a range of 20 to 200.

(6) The carbon fiber nonwoven fabric according to any of (1), (3) to (5), wherein the aliphatic compound having a plurality of epoxy groups is at least one kind of compound selected from glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyethylene glycol diglycidyl ether group and polypropylene glycol diglycidyl ether group.

(7) The carbon fiber nonwoven fabric according to (2), wherein the aromatic compound having a plurality of epoxy groups in which a number of atoms present between an epoxy group and an aromatic ring is 6 or more is a compound shown in the following chemical formula 1.

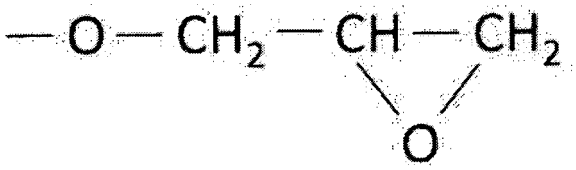
[Chemical formula 1]



[I]

(Where, R^1 in formula [I] is the following chemical formula 2,

[Chemical formula 2]



[II]

R^2 represents an alkylene group having a carbon number of 2 to 30, R^3 is -H or $-CH_3$, m and n represent an integer of 2 to 48, and m + n is in a range of 4 to 50.)

(8) The carbon fiber nonwoven fabric according to (7), wherein the R^2 is $-CH_2CH_2-$ or $-CH(CH_3)\,CH_2-$.

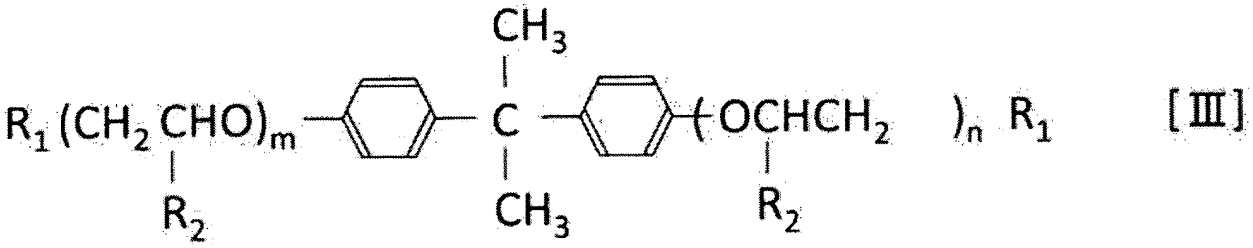
(9) The carbon fiber nonwoven fabric according to (2), wherein the aromatic compound is a condensed polycyclic aromatic compound.

(10) The carbon fiber nonwoven fabric according to (9), wherein a skeletal structure of the condensed polycyclic aromatic compound is naphthalene, anthracene, phenanthrene or pyrene.

(11) A carbon fiber nonwoven fabric including carbon fibers, characterized in that at least one kind of compound selected from chemical formulae (III), (IV) and (V) shown in the following chemical formula 3 to chemical formula 5 is made adhere to the carbon fibers at an amount of 0.1 to 5.0 wt.% relative to the weight of the carbon fibers of 100 wt.%, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers

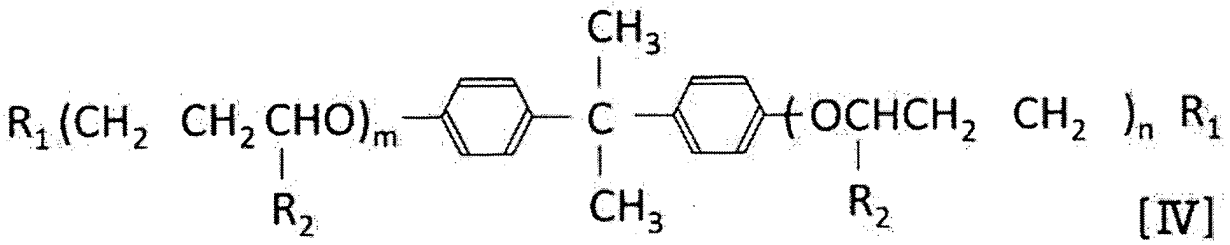
forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000 fibers per bundle among carbon fiber bundles in the carbon fiber nonwoven fabric, and a standard deviation σ of the number of carbon fibers forming the carbon fiber bundle (1) is in a range of 50 to 500.

[Chemical formula 3]



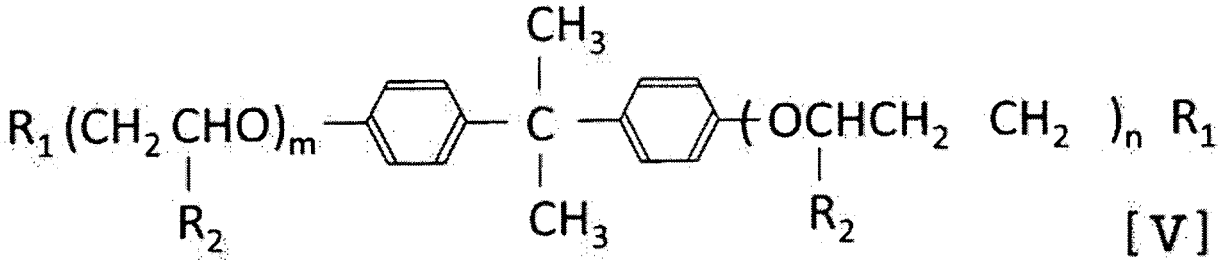
[III]

[Chemical formula 4]



[IV]

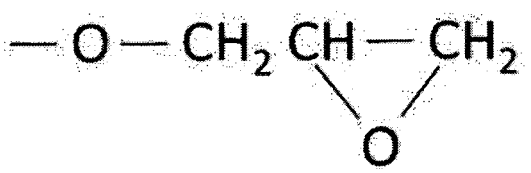
[Chemical formula 5]



[V]

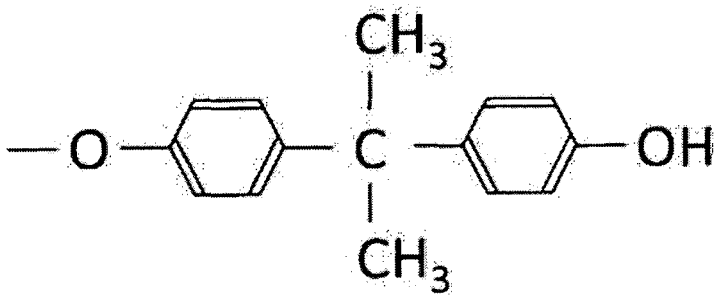
In the above-described formulae, R_1 represents H, OH, the following chemical formula 6 or the following chemical formula 7, R_2 represents H or OH, m and n represent an integer of 1 to 49, and m + n is in a range of 10 to 50.

[Chemical formula 6]



[VI]

[Chemical formula 7]



[VII]

(12) The carbon fiber nonwoven fabric according to any of (1) to (11), wherein the standard deviation σ of the number of carbon fibers forming the carbon fiber bundle (1) is in a range of 50 to 350.
(13) The carbon fiber nonwoven fabric according to any of (1) to (12), wherein a proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers is in a range of 5 to 80 wt.%.
(14) The carbon fiber nonwoven fabric according to any of (1) to (13), wherein the carbon fiber nonwoven fabric is formed from a carbon fiber bundle whose drape value (cm)/single fiber flexural stiffness ($Pa \cdot cm^4$) at 25°C is in a range of 1.4×10^3 to 4.0×10^3 ($cm/(Pa \cdot cm^4)$).
(15) The carbon fiber nonwoven fabric according to any of (1) to (14), wherein a single fiber flexural stiffness of carbon fibers forming the carbon fiber nonwoven fabric is in a range of 1.0×10^{-11} to 2.8×10^{-11} ($Pa \cdot cm^4$).
(16) The carbon fiber nonwoven fabric according to any of (1) to (15), wherein a fiber length Ln of carbon fibers forming the carbon fiber nonwoven fabric is in a range of 3 to 50 mm.

[0008] In such a carbon fiber nonwoven fabric according to the present invention, by satisfying the above-described ranges specified in the present invention, as shown in the results of Examples described later, a high flowability at the time of molding using it can be obtained as well as high mechanical properties of a molded article can be realized, the variability in the mechanical properties is small, and besides, an excellent shaping property can be exhibited. Further, in order to satisfy both of the high flowability and the high mechanical properties more securely, as described above, can be employed preferred compound, standard deviation σ of the number of carbon fibers, range of the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers, range of the drape value (cm)/single fiber flexural stiffness ($Pa \cdot cm^4$), range of the single fiber flexural stiffness of carbon fibers, etc.

Effect according to the Invention

[0009] Thus, in the carbon fiber nonwoven fabric according to the present invention, a carbon fiber nonwoven fabric can be provided wherein, when a carbon fiber composite material is molded using the same, high flowability and high mechanical properties can be both achieved, the variability in the mechanical properties is small, and the carbon fiber followability to a small portion is also excellent.

Brief explanation of the drawings

[0010]

[Fig. 1] Fig. 1 is a schematic diagram showing an example of a carding machine.
[Fig. 2] Fig. 2 is a schematic diagram showing an example of an air laid machine.
[Fig. 3] Fig. 3 is a schematic diagram of a measurement device showing a determination method of a drape value.

Embodiments for carrying out the Invention

[0011] Hereinafter, the present invention will be explained in detail together with Examples and Comparative Examples.
[0012] First, although the carbon fibers used in the present invention are not particularly restricted, high-strength and high-elastic modulus carbon fibers can be used, and one kind of carbon fibers may be used or two or more kinds of carbon fibers may be used together. In particular, PAN-based, pitch-based and rayon-based carbon fibers can be exemplified. From the viewpoint of the balance between the strength and the elastic modulus of a molded article to be obtained, PAN-based carbon fibers are more preferable. The density of carbon fibers is preferably in a range of 1.65 to 1.95 g/cm^3, and more preferably in a range of 1.70 to 1.85 g/cm^3. If the density is too high, the lightness in weight of a

carbon fiber-reinforced plastic obtained is poor, and if too low, there is a case where the mechanical properties of a carbon fiber-reinforced plastic obtained become low.

[0013] Further, the carbon fibers are preferably formed as a bundle from the viewpoint of productivity, and it is preferred that the number of single fibers in the bundle is many. The number of single fibers for the carbon fiber bundle can be employed within a range of 1,000 to 350,000, and in particular, it is preferably employed within a range of 10,000 to 100,000.

[0014] The single fiber flexural stiffness of carbon fibers is preferably in a range of 1.0×10^{-11} to 2.8×10^{-11} ($Pa \cdot cm^4$), and more preferably in a range of 1.0×10^{-11} to 1.5×10^{-11} ($Pa \cdot cm^4$). By the condition where the single fiber flexural stiffness is in the above-described range, in the process for manufacturing a carbon fiber nonwoven fabric described later, it makes possible to stabilize the quality of carbon fiber nonwoven fabric obtained.

[0015] For the purpose of improving the adhesive property between carbon fibers and a matrix resin when a carbon fiber composite material is molded, it is preferred that the carbon fibers are surface treated. As the method of the surface treatment, there are electrolytic treatment, ozone treatment, ultraviolet treatment, etc.

[0016] Then, in a carbon fiber nonwoven fabric according to the first embodiment of the present invention, the carbon fibers are sized with an aliphatic compound having a plurality of epoxy groups. The aliphatic compound in the present invention means a noncyclic straight-chain saturated hydrocarbon, a branched-chain saturated hydrocarbon, a noncyclic straight-chain unsaturated hydrocarbon, a branched-chain unsaturated hydrocarbon, or a chain-structure compound substituting oxygen atom (O), nitrogen atom (NH, N), sulfur atom (SO_3H, SH) or carbonyl atomic group (CO) for the carbon atom of the above-described hydrocarbons (CH_3, CH_2, CH, C).

[0017] Further, it is preferred that the above-described compound having a plurality of epoxy groups is a compound having an epoxy group at each end of the longest atomic chain, in particular, a compound having an epoxy group only at each end of the longest atomic chain. In the present invention, in a compound having a plurality of epoxy groups, an atomic chain having the greatest total number of atoms among the total numbers of carbon atoms and heteroatoms (oxygen atom, nitrogen atom, etc.) forming respective chain structures which link between two epoxy groups is defined as the longest atomic chain, and the total number of atoms forming the longest atomic chain is defined as a number of atoms of the longest atomic chain. Where, the number of atoms such as hydrogen linked to the atoms forming the longest atomic chain is not included to the total number.

[0018] Although the structure of a side chain is not particularly restricted, a structure hard to become a crosslinking point is preferred in order to prevent that a density of crosslinking between molecules of a compound of a sizing agent becomes too great.

[0019] If the number of epoxy groups in a compound of a sizing agent is less than 2, it cannot be done to effectively bridge between carbon fibers and a matrix resin. Therefore, the number of epoxy groups is necessary to be two or more in order to effectively bridge between carbon fibers and a matrix resin.

[0020] On the other hand, if the number of epoxy groups is too large, because the density of crosslinking between molecules of a compound of a sizing agent becomes great and it causes a brittle sizing layer and as a result a tensile strength of a composite is reduced, the number of epoxy groups is preferably 6 or less, more preferably 4 or less, and further preferably, it is 2. Furthermore, it is more preferred that these two epoxy groups are present at both ends of the longest atomic chain. Namely, by the presence of the epoxy groups at both ends of the longest atomic chain, because it is prevented that a local density of crosslinking increases, such a structure is preferred for a tensile strength of a composite.

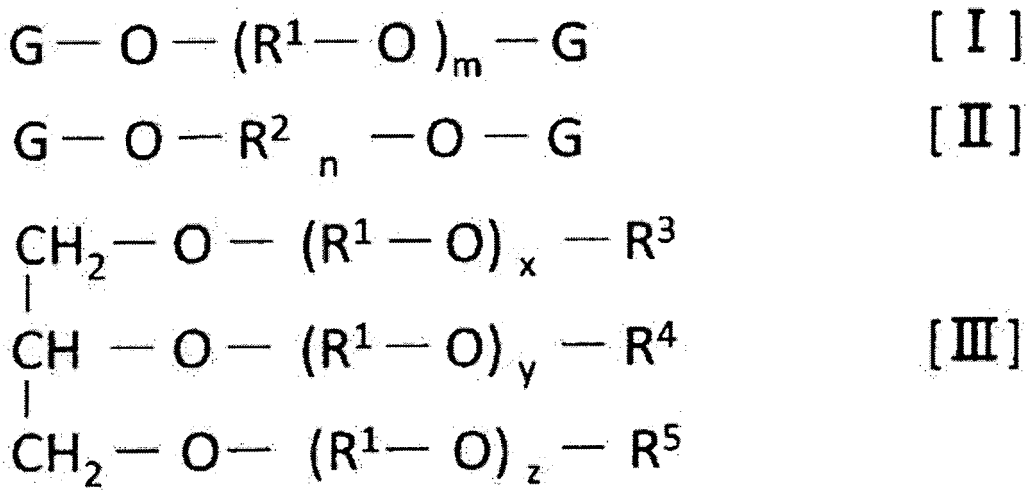
[0021] As a structure of the epoxy group, a glycidyl group having a high reactivity is preferred.

[0022] The molecular weight of such an aliphatic compound is preferably 80 or more and 3,200 or less, more preferably 100 or more and 1,500 or less, and further preferably 200 or more and 1,000 or less, from the viewpoint of preventing deterioration of handling ability as a sizing agent caused by a condition that the resin viscosity is too low or too high.

[0023] As concrete examples of the aliphatic compound having a plurality of epoxy groups in the present invention, for example, as diglycidyl ether compounds, can be exemplified ethylene glycol diglycidyl ether and polyethylene glycol diglycidyl ether group, propylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether group, 1,4-butanediol diglycidyl ether, neopentyl glycol diglycidyl ether, polytetramethylene glycol diglycidyl ether, polyalkylene glycol diglycidyl ether group, etc. Further, as polyglycidyl ether compounds, can be exemplified glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether group, sorbitol polyglycidyl ether group, arabitol polyglycidyl ether group, trimethylol propane polyglycidyl ether group, pentaerythritol polyglycidyl ether group, polyglycidyl ether group of aliphatic polyatomic alcohol, etc.

[0024] Preferably, it is a polyglycidyl ether compound having a glycidyl group high in reactivity. Further preferably, polyethylene glycol diglycidyl ether group, polypropylene glycol diglycidyl ether group, alkane diol diglycidyl ether group, and compounds having the following structures, are preferred.

[Chemical formula 8]



[0025] Where, G represents a glycidyl group, R^1 represents $-CH_2CH_2-$, $-CH_2CH_2CH_2-$ or $-CH(CH_3)CH_2-$, R^2 represents $-CH_2-$, at least two of R^3, R^4 and R^5 represent -G and the other represents -H or -G, m represents an integer of 1 to 25, n represents an integer of 2 to 75, x, y and z represent zero or a positive integer, and x + y + z is preferably in a range of 0 to 25. Further, a mixture of these compounds may be used.

[0026] In the aliphatic compound having a plurality of epoxy groups, it is preferred that the number of atoms of the longest atomic chain is 20 or more. Namely, if the number of atoms is less than 20, there is a possibility that the density of crosslinking in the sizing layer becomes high and therefore it is likely to become a structure low in toughness, and as a result, a tensile strength of a composite is hard to be exhibited. To the contrary, if the number of atoms of the longest atomic chain is greater, because the sizing layer is flexible and is likely to become a structure high in toughness, as a result, a tensile strength of a composite is liable to be increased, and in particular, because there is a feature that a tensile strength in case of a brittle resin is high, more preferably, the number of atoms of the longest atomic chain is 25 or more, and further preferably, 30 or more.

[0027] However, the greater the number of atoms of the longest atomic chain is, more flexible the structure becomes, but if too long, there is a possibility that the chain is bent and a functional group is sequestered and as a result, the adhesive property between carbon fibers and a resin is reduced, the number of atoms is preferably 200 or less, more preferably 100 or less.

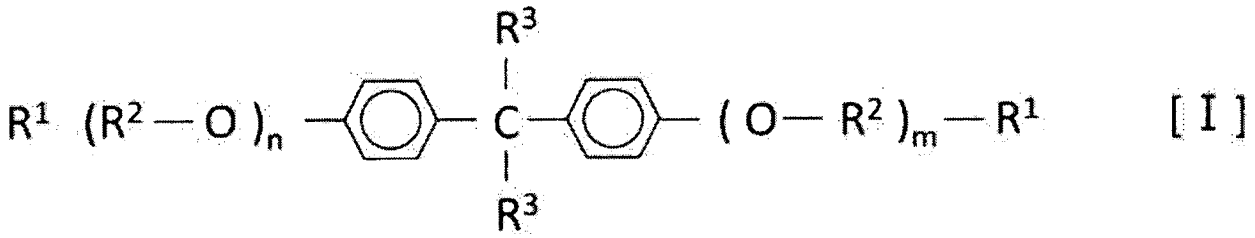
[0028] In case where the aliphatic compound contains a cyclic aliphatic skeletal structure, if the epoxy group is sufficiently apart from the cyclic skeletal structure, concretely, if apart from by 6 or more in number of atoms, it can be used.

[0029] In a carbon fiber nonwoven fabric according to the second embodiment of the present invention, an aromatic compound having a plurality of epoxy groups in which a number of atoms present between an epoxy group and an aromatic ring is 6 or more is used as the sizing agent. The "number of atoms present between an epoxy group and an aromatic ring" means the total number of carbon atoms, heteroatoms (oxygen atom, nitrogen atom, etc.) and carbonyl atomic groups forming chain structures which link between the epoxy group and the aromatic ring.

[0030] If the number of atoms present between an epoxy group and an aromatic ring is less than 6 as the sizing agent, because a rigid and three-dimensionally large compound is interposed at an interface between carbon fibers and a matrix resin, the reactivity with a surface functional group present on the outermost surfaces of carbon fibers is not improved, and as a result, improvement of the properties in the lateral direction of a composite material cannot be expected.

[0031] Concretely, a compound shown in the following formula [I] (chemical formula 9) can be exemplified.

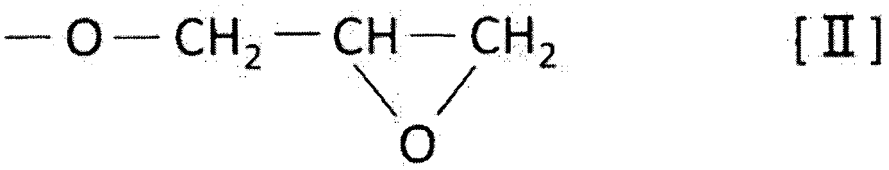
[Chemical formula 9]



[I]

[0032] (Where, R^1 in the formula [I] represents the following chemical formula 10,

[Chemical formula 10]



[II]

[0033] R^2 represents an alkylene group having a carbon number of 2 to 30, R^3 is -H or $-CH_3$, m and n represent an integer of 2 to 48, and m + n is in a range of 4 to 50.)

[0034] In this case, it is preferred the molecular chain of the compound is straight chain like having a flexibility and the molecular weight thereof is small so as not to interpose a rigid and three-dimensionally large compound at an interface between carbon fibers and a matrix resin in a carbon fiber composite material, and therefore, each of the above-described m, n is 2 or more, preferably 3 or more, further preferably 5 or more, and the above-described m + n is 4 or more, preferably 6 or more, further preferably 10 or more. In a compound in which each of m, n is less than 2 or m + n is less than 4, there is a possibility that the adhesive property between a matrix resin and carbon fibers, which is a purpose of the present invention, is reduced. On the other hand, if m + n exceeds 50, there is a possibility that the compatibility with a matrix resin is reduced and the adhesive property between a matrix resin and carbon fibers is reduced. Further, in the formula [I], it is preferred that R^2 is $-CH_2CH_2-$ or $CH(CH_3)CH_2-$.

[0035] Here, the bisphenol A part or B part has an advantage for improving the compatibility with a matrix resin and an advantage for improving the fluff resistance.

[0036] In the above description, the skeletal structure of the aromatic compound having a plurality of epoxy groups in which a number of atoms present between an epoxy group and an aromatic ring is 6 or more may also be a condensed polycyclic aromatic compound. As the skeletal structure of the condensed polycyclic aromatic compound, for example, naphthalene, anthracene, phenanthrene, chrysene, pyrene, naphthacene, triphenylene, 1,2-benzanthracene, benzopyrene, etc. can be exemplified. Desirably, naphthalene, anthracene, phenanthrene and pyrene, whose skeletal structures are small, are preferred.

[0037] The epoxy equivalent of the condensed polycyclic aromatic compound having a plurality of epoxy groups is preferably in a range of 150 to 350, more preferably in a range of 200 to 300, from the viewpoint of obtaining an advantage for improving the adhesive property sufficiently.

[0038] The molecular weight of the condensed polycyclic aromatic compound having a plurality of epoxy groups is preferably in a range of 400 to 800, more preferably in a range of 400 to 600, from the viewpoint of preventing deterioration of handling ability as a sizing agent caused by increase of the resin viscosity.

[0039] Further, to the above-described sizing agent, the other components such as a bisphenol-type epoxy compound having a small molecular weight such as "Epikote" 828 or "Epikote" 834, a straight-chain like low molecular weight epoxy compound, polyethylene glycol, polyurethane, a polyester, an emulsifier or a surfactant, may be added, for the purpose of adjustment of viscosity, improvement of abrasion resistance, improvement of fluff resistance, improvement of convergence of fibers, improvement of higher-order processability, etc.

[0040] Furthermore, there is no problem even in adding a rubber such as nitrile-butadiene rubber, a straight-chain like epoxy modified compound having an elastomer property such as epoxy end group nitrile-butadiene rubber, etc.

[0041] The adhesion amount of the sizing agent to carbon fibers is preferably 0.01 wt.% or more and 10 wt.% or less per unit weight of carbon fibers, more preferably 0.05 wt.% or more and 5 wt.% or less, further preferably 0.1 wt.% or more and 2 wt.% or less, from the viewpoint of making the width of improvement of adhesive property with a resin while preventing the sizing agent from being consumed excessively.

[0042] In the present invention, it is preferred that the sizing agent is uniformly coated. Namely, it is preferred that the thickness of the sizing agent layer is in a range of 20 to 200 angstroms and the maximum value of the thickness does not exceed two times of the minimum value. By such a uniform sizing agent layer, a coupling effect can be exhibited more effectively.

[0043] In a carbon fiber nonwoven fabric according to the third embodiment of the present invention, at least one kind of a specified compound selected from the aforementioned chemical formulae (III), (IV) and (V) (hereinafter, also referred to as merely "a sizing agent") is made adhere to the carbon fibers of the carbon fiber nonwoven fabric at an amount of 0.1 to 5.0 wt.% relative to the weight of the carbon fibers of 100 wt.%. Polyethylene oxide part or polypropylene oxide part in such a compound gives a smoothness to carbon fibers, exhibits an effect for reducing a friction force, and when formed to a carbon fiber nonwoven fabric described later, a friction force caused by tangle of carbon fibers to each other can be reduced, thereby improving the flowability and the formability. On the other hand, bisphenol A part has an effect for improving the compatibility with a matrix resin. By using the above-described respective components at a condition being copolymerized, the compatibility with a resin can be maintained as compared with a case where the respective single components are used at a condition being mixed, and the effect for reducing a coefficient of friction can be exhibited further greatly.

[0044] Further, in the above-described sizing agent, in a compound in which m + n in the aforementioned chemical formula is less than 10, an effect for reducing a coefficient of friction is poor, and such a compound is not preferred. Further, if m + n exceeds 50, because the compatibility with a matrix resin is reduced and the adhesive property between the matrix resin and carbon fibers is reduced, such a compound is not preferred.

[0045] As the treatment using such a sizing agent, generally a treatment method can be employed wherein a liquid containing a sizing agent (sizing liquid) is made adhere after water wet carbon fiber bundles having a moisture content of approximately 20 to 80 wt.%, wetted with water in known surface treatment process and water washing process, are dried.

[0046] Although the method for providing a sizing agent is not particularly limited, for example, there are a method for dipping carbon fibers in a sizing liquid via rollers, a method for bringing carbon fibers into contact with rollers adhered with a sizing liquid, a method for spraying an atomized sizing liquid, etc. Further, although the method may be any of batch type and continuous type, continuous type good in productivity and small in unevenness is preferred. In this connection, it is preferred to control the concentration and temperature of the sizing liquid, yarn tension, etc., so that the adhesion amount of sizing agent effective component relative to carbon fibers becomes uniform. Further, it is more preferred to vibrate carbon fibers with a ultrasonic wave when the sizing agent is provided.

[0047] Although the drying temperature and the drying time should be adjusted depending upon the adhesion amount of the compound, the drying temperature is preferably 130°C or higher and 350°C or lower, and more preferably 180°C or higher and 250°C or lower, from the viewpoints of completely removing a solvent used for providing the sizing agent, shortening the time required for drying, on the other hand, preventing thermal deterioration of the sizing agent and preventing deterioration of the spreading property of carbon fiber bundles caused by the bundles being hardened.

[0048] As the solvent used for the sizing agent, although water, methanol, ethanol, dimethyl formamide, dimethyl acetamide, acetone, etc. can be exemplified, water is preferred from the viewpoints of easy handling ability and disaster prevention. Therefore, in case where a compound insoluble or slightly soluble in water is used as a sizing agent, it is preferred to use it after making it water dispersible by adding an emulsifier, a surfactant, etc. Concretely, as the emulsifier or the surfactant, can be used anionic emulsifiers such as styrene-maleic anhydride copolymer, olefin-maleic anhydride copolymer, formalin condensate of naphthalene sulfonate and polyacrylic soda, cationic emulsifiers such as polyethylene imine and polyvinyl imidazoline, nonionic emulsifiers such as nonyl phenol ethylene oxide adduct, polyvinyl alcohol, copolymer of polyoxyethylene ether ester and sorbitan ester ethyl oxide adduct, and nonionic emulsifiers small in interaction with epoxy groups are preferred.

[0049] The adhesion amount of a sizing agent relative to the mass of only the carbon fibers is preferably 0.01 mass% or more and 10 mass% or less, more preferably 0.05 mass% or more and 5 mass% or less, and further preferably 0.1 mass% or more and 2 mass% or less. If less than 0.01 mass%, the effect for improving the adhesive property is hardly exhibited. If more than 10 mass%, there is a possibility that the mechanical properties when the carbon fiber nonwoven fabric is made into a molded article of a carbon fiber composite material may be reduced.

[0050] For the carbon fiber bundles, in order to obtain the carbon fiber aggregates described later, the drape value/ single fiber flexural stiffness, determined by dividing the drape value, that is an index representing the hardness of the carbon fiber bundle, with the single fiber flexural stiffness, is preferably in a range of 1.4×10^3 to 4.0×10^3 cm/(Pa· cm^4), and more preferably in a range of 1.5×10^3 to 3.0×10^3 cm/(Pa· cm^4). If the drape value/ single fiber flexural stiffness is less than 1.4×10^3 cm/(Pa· cm^4), the convergence of the fibers is poor, in the process for preparing the carbon fiber aggregates such as air laid or carding described later, the fibers are liable to be spread, there is a possibility that the moldability deteriorates when made into a carbon fiber composite material, and if it exceeds 4.0×10^3 cm/(Pa· cm^4), there is a possibility that the wettability with a matrix resin deteriorates and the mechanical properties are reduced when made into a carbon fiber composite material.

[0051] As the process for obtaining carbon fiber aggregates, a process such as carding or air laid can be exemplified. The carding mentioned in the present invention means an operation for arranging the direction of discontinuous fibers or spreading fibers by applying a force in an approximately same direction to the aggregates of discontinuous fibers with a comb-like member. Generally, it is performed using a carding machine equipped with a roll having many needle-like projections on the surface and/or a roll wound with a metallic wire having saw blade-like projections.

[0052] When such a carding is carried out, it is preferred to control the time (residing time), during which carbon fibers reside in the carding machine, to be short, for the purpose of preventing the carbon fibers from being folded. Concretely, it is preferred to transfer the carbon fibers existing on the wires wound onto a cylinder roll of the carding machine to a doffer roll in a time as short as possible. Therefore, in order to accelerate such a transfer, it is preferred to rotate the cylinder roll at a high rotational speed, for example, such as 150 rpm or higher. Further, from a similar reason, the surface speed of the doffer roll is preferably a high speed, for example, such as 10 m/min. or higher.

[0053] The process for carding the carbon fiber bundles is not particularly restricted, and a general one can be used. For example, as shown in Fig. 1, a carding machine 1 mainly comprises a cylinder roll 2, a take-in roll 3 provided at an upstream side and closely to the outer circumferential surface of the cylinder roll 2, a doffer roll 4 provided closely to the outer circumferential surface of the cylinder roll 2 at a downstream side which is a side opposite to the side of the take-in roll 3, a plurality of worker rolls 5 provided closely to the outer circumferential surface of the cylinder roll 2 between the take-in roll 3 and the doffer roll 4, stripper rolls 6 provided closely to the worker rolls 5, and a feed roll 7 provided closely to the take-in roll 3, and a belt conveyer 8.

[0054] Discontinuous carbon fiber bundles 9 are supplied to belt conveyer 8, and the carbon fiber bundles 9 are introduced onto the outer circumferential surface of cylinder roll 2 through the outer circumferential surface of feed roll 7 and then through the outer circumferential surface of take-in roll 3. Up to this stage, the carbon fiber bundles are spread and become floc-like aggregates of carbon fiber bundles. Although a part of the floc-like aggregates of carbon fiber bundles introduced onto the outer circumferential surface of cylinder roll 2 wind around the outer circumferential surfaces of worker rolls 5, these carbon fibers are stripped off by stripper rolls 6 and returned again onto the outer circumferential surface of the cylinder roll 2. Many needles, projections exist at standing conditions on the outer circumferential surfaces of the respective rolls of feed roll 7, take-in roll 3, cylinder roll 2, worker rolls 5 and stripper rolls 6, and in the above-described steps, by the operation of the needles, the carbon fiber bundles are spread into predetermined-condition bundles, and oriented to some extent. The carbon fiber bundles, spread into predetermined-condition bundles through such steps, move onto the outer circumferential surface of doffer roll 4 as a sheet-like web 10 which is one form of the carbon fiber aggregates.

[0055] Air laid is a process for producing a nonwoven fabric sheet of short fibers, it is not particularly restricted, and a general one can be used. As general air laid processes, can be exemplified Honshu Paper process, Kroyer process, Danweb process, J&J process, KC process, Scott process, etc.

[0056] For example, as shown in Fig. 2, air laid machine 11 has drums 12 rotated in directions reverse to each other, each formed in a cylinder shape and having small holes, and pin cylinders 13 provided in the respective drums 12. Carbon fiber bundle single materials or carbon fiber bundles and thermoplastic resin fibers are air transported to drums 12 together with a large amount of air, they are spread by pin cylinders 13 in drums 12, discharged from the small holes, and they drop onto wires 14 running thereunder. Where, the air used for the air transportation is sucked into a suction box 15 provided under wires 14, and only spread carbon fiber bundle single materials or spread carbon fiber bundles and thermoplastic resin fibers are left on wires 14 to form a carbon fiber nonwoven fabric.

[0057] Further, the carbon fiber nonwoven fabric indicated here means a fabric which is kept in form by tangle or friction of fibers to each other at a condition where discontinuous carbon fiber bundles are spread and oriented by the above-described carding or air laid, and can be exemplified a thin sheet-like web, a nonwoven fabric obtained by laminating webs, as needed, by tangle or adhesion, etc. From the viewpoint of preventing carbon fibers from being folded or bent and suppressing the tangle force pf fibers to each other to achieve a good flowability when made into a carbon fiber composite material, the carbon fiber nonwoven fabric is obtained preferably by air laid, and from the viewpoint of uniformity of nonwoven fabric, it is obtained preferably by carding.

[0058] Although the carbon fiber nonwoven fabric may be formed by only carbon fibers, thermoplastic resin fibers and/or thermoplastic resin particles can also be contained. It is preferred to add thermoplastic resin fibers because breakage of carbon fibers at the process of air laid or carding can be prevented. Because carbon fibers are rigid and fragile, they are hard to be tangled and liable to be broken. Therefore, there is a problem in the carbon fiber nonwoven fabric formed by only carbon fibers that during the production, the fabric is easily cut or the carbon fibers are liable to be fallen off. In the air laid process, by containing thermoplastic resin fibers and/or thermoplastic resin particles, the handling ability of the carbon fiber nonwoven fabric can be improved by carrying out a method for thermally fusing them by pressing or heat treatment due to thermal calender rollers or thermal emboss rollers or a method for tangling the fibers by needle punch or water jet needle, etc., employed at a later step. In the carding process, by containing thermoplastic resin fibers which are flexible and hard to be broken and liable to be tangled, carbon fiber aggregates high in uniformity can be formed. In the present invention, in case where thermoplastic resin fibers are contained in carbon fiber

aggregates, the content of carbon fibers in the carbon fiber aggregates is preferably in a range of 20 to 95 mass%, more preferably in a range of 50 to 95 mass%, and further preferably in a range of 70 to 95 mass%. If the rate of carbon fibers is low, it becomes difficult to obtain high mechanical properties when made into a carbon fiber composite material, and to the contrary, if the rate of thermoplastic resin fibers is too low, the above-described advantage for improving uniformity of the carbon fiber aggregates cannot be obtained.

[0059] As to the carbon fiber bundles in the carbon fiber nonwoven fabric, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000. From the viewpoint of improving the carbon fiber strength utilization factor and the surface appearance of a molded article when made into a carbon fiber composite material described later, the number average x of carbon fibers forming the bundle is preferably in a range of 90 to 600, more preferably in a range of 90 to 500. From the viewpoint of increasing the content of carbon fibers when made into a carbon fiber composite material and obtaining a high elastic modulus, the number average x is preferably in a range of 300 to 1,000, more preferably in a range of 500 to 1,000. If the number average x of carbon fibers of the carbon fiber bundles is less than 90, the number of tangles of fibers to each other increases, and the flowability deteriorates. If more than 1,000, the mechanical properties and the followability of carbon fibers to small parts deteriorate, and the variability in mechanical properties becomes great.

[0060] As to the carbon fiber bundles in the carbon fiber nonwoven fabric, it is preferred that a proportion of the carbon fiber bundles (1), in which the number of carbon fibers forming a carbon fiber bundle is 90 or more, relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric is 5 wt.% or more and 80 wt.% or less. From the viewpoint of improving the carbon fiber strength utilization factor and the surface appearance of a molded article, it is preferably 5 wt.% or more and 50 wt.% or less, further preferably 5 wt.% or more and 45 wt.% or less. From the viewpoints of further improving the flowability, increasing the content of carbon fibers when made into a carbon fiber composite material and obtaining a high elastic modulus, it is preferably more than 30 wt.% and 80 wt.% or less, further preferably more than 35 wt.% and 80 wt.% or less. From the viewpoint of balance of the carbon fiber strength utilization factor, the surface appearance of a molded article and the flowability, it is preferably more than 30 wt.% and 50 wt.% or less. If the proportion of the carbon fiber bundles (1) is less than 5 wt.%, the number of tangles of fibers to each other increases, and the flowability deteriorates. If more than 80 wt.%, the mechanical properties and the followability of carbon fibers to small parts deteriorate, and the variability in mechanical properties becomes great.

[0061] By the condition where a standard deviation σ of the number x_n of carbon fibers forming the above-described carbon fiber bundle (1) in the carbon fiber nonwoven fabric satisfies a range of $50 \leqq \sigma \leqq 500$ and the carbon fiber bundles are distributed in the carbon fiber nonwoven fabric by being dispersed, a carbon fiber nonwoven fabric can be obtained in which high flowability and mechanical properties can be both satisfied, the variability in mechanical properties is small, and which is excellent also in followability of carbon fibers to small parts. If the above-described standard deviation σ is less than 50, the flowability deteriorates, and if the above-described standard deviation σ is more than 500, the mechanical properties deteriorate and the variability in mechanical properties becomes great. The above-described standard deviation σ is preferably in a range of $100 \leqq \sigma \leqq 350$, more preferably in a range of $150 \leqq \sigma \leqq 350$, and further preferably in a range of $150 \leqq \sigma \leqq 300$.

[0062] In the present invention, in case where thermoplastic resin fibers are contained in the carbon fiber aggregates, the fiber length of the thermoplastic resin fibers is not particularly limited as long as it is in a range capable of achieving the objective of the present invention such as keeping the form of the carbon fiber aggregate or preventing falling off of carbon fibers, and generally, thermoplastic resin fibers having a length of approximately 3 to 100 mm can be used. Where, it is also possible to decide the fiber length of thermoplastic resin fibers relatively in accordance with the fiber length of carbon fibers.

[0063] Further, in the above-described carding, it is preferred to provide a crimp to the thermoplastic resin fibers for the purpose of enhancing the effect of tangle due to the thermoplastic resin fibers. The degree of the crimp is not particularly limited as long as it is in a range capable of achieving the objective of the present invention, and generally, thermoplastic resin fibers having a number of crimps in a range of approximately 5 to 25 crests per 25 mm and a rate of crimp in a range of approximately 3 to 30% can be used.

[0064] In case where thermoplastic resin particles are contained in the carbon fiber aggregates, as the shape of the thermoplastic resin particles, a spherical shape, a small piece-like shape, and columnar shape such as a pellet, can be exemplified. In case of a spherical shape, the preferable average particle diameter is in a range of 0.01 to 1,000 μm.

[0065] The material for the above-described thermoplastic resin fibers is not particularly restricted, and it can be appropriately selected from a range that does not greatly reduce the mechanical properties of a carbon fiber composite material. For example, fibers can be used which are prepared by spinning a resin such as a polyolefin-group resin such as polyethylene or polypropylene, a polyamide-group resin such as nylon 6 or nylon 6,6, a polyester-group resin such as polyethylene terephthalate or polybutylene terephthalate, a polyetherketone, a polyethersulfone or an aromatic polyamide. It is preferred that such a material for thermoplastic resin fibers is appropriately selected in accordance with the combination with a matrix resin. In particular, thermoplastic resin fibers prepared using the same resin as a matrix resin, a resin having a compatibility with a matrix resin or a resin having a high adhesive property with a matrix resin is preferred,

because the mechanical properties of a carbon fiber-reinforced plastic are not lowered. For example, the thermoplastic resin fibers are preferred to be composed of at least one kind of fibers selected from the group consisting of polyamide fibers, polyphenylene sulfide fibers, polypropylene fibers, polyetheretherketone fibers and phenoxy resin fibers.

[0066] In the present invention, when a matrix resin is impregnated into the carbon fiber nonwoven fabric, a method may be employed wherein carbon fiber nonwoven fabric containing thermoplastic resin fibers is prepared and the thermoplastic resin fibers contained in the carbon fiber nonwoven fabric are used as the matrix resin as they are, or a method may also be employed wherein carbon fiber nonwoven fabric not containing thermoplastic resin fibers is used as a raw material, and a matrix resin is impregnated at an arbitrary stage for producing a carbon fiber composite material. Further, even in case where the carbon fiber nonwoven fabric containing thermoplastic resin fibers is used as the raw material, a matrix resin can be impregnated at an arbitrary stage for producing a carbon fiber composite material. In such a case, a resin forming thermoplastic resin fibers and a matrix resin may be an identical resin, or may be resins different from each other. In case where the resin forming thermoplastic resin fibers and the matrix resin are different from each other, it is preferred that both resins have a compatibility or a high affinity.

[0067] When the carbon fiber composite material is produced, a thermoplastic resin as a matrix resin is impregnated into the above-described carbon fiber nonwoven fabric, and the impregnation step for manufacturing the carbon fiber composite material can be carried out using a press machine having a heating function. The press machine is not particularly restricted as long as it can realize temperature and pressure required for the impregnation of the matrix resin, a usual press machine having a plane-like platen moved vertically, or a so-called double belt press machine having a mechanism for running a pair of endless steel belts can be used. In such an impregnation step, after the matrix resin is prepared in a sheet-like form such as a film, a nonwoven fabric or a woven fabric, it is laminated with the carbon fiber nonwoven fabric, and at that condition, the matrix resin can be melted and impregnated using the above-described press machine and the like. Further, a method can also be employed wherein discontinuous fibers are prepared using a matrix resin, by mixing them and inorganic fibers at a step for making a carbon fiber nonwoven fabric, a carbon fiber nonwoven fabric containing the matrix resin and the inorganic fibers is prepared, and this carbon fiber nonwoven fabric is heated and pressed using the press machine and the like.

[0068] Next, Examples and Comparative Examples of the present invention will be explained.

[0069] First, the properties and determination methods used in the Examples and Comparative Examples will be explained.

(1) Method for determining fiber bundles:

[0070] A sample with a size of 100 mm x 100 mm was cut out from a carbon fiber nonwoven fabric, and thereafter, the sample was heated in an electric furnace heated at 500°C for about one hour to burn off organic substances such as thermoplastic resin fibers. After the mass of carbon fiber nonwoven fabric left after cooled down to a room temperature was determined, carbon fiber bundles were all extracted from the carbon fiber nonwoven fabric by a pincette. With respect to all the extracted carbon fiber bundles, using a balance capable of measuring up to a degree of 1/10,000g, the weight Mn and the length Ln of each carbon fiber bundle is determined. After the determination, for each bundle, the number of single fibers of carbon fibers forming the carbon fiber bundle x_n = Mn/(Ln x F) is calculated. Where, F is a fineness of carbon fibers, and x_n is a number of single fibers forming the carbon fiber bundle. The determination is carried out at a condition where carbon fiber bundles, in each of which the number of single fibers of carbon fibers forming the carbon fiber bundle x_n is 90 or more, are referred to as carbon fiber bundles (1), the total weight is referred to as M_1 and the total number of bundles is referred to as N. Further, the determination is carried out at a condition where carbon fiber bundles, in each of which the number of single fibers of carbon fibers forming the bundle is less than 90, are referred to as fiber bundles (2), and the total weight of the carbon fiber bundles (2) is referred to as M_2. For fiber bundles spread to a degree at which the bundles cannot be extracted by a pincette, the weight thereof was determined in the lump at the last. Further, in case where the fiber length is small and the determination of weight becomes difficult, the fiber lengths may be classified at an interval of about 0.2 mm and the weights of a plurality of classified bundles may be determined in the lump, and an average value thereof may be used. After classifying and determining all bundles, a number average x of carbon fibers forming the carbon fiber bundle (1) = $\sum\{Mn/(Ln \times F)\}/N$ and a standard deviation σ of the number x_n of carbon fibers forming the carbon fiber bundle = $\{1/N \times \sum(x_n - x)^2\}^{1/2}$ are calculated, and the average value X of Mn/Ln of carbon fiber bundles (1), the number average x of carbon fibers forming the bundle and the standard deviation σ of the number x_n of carbon fibers forming the carbon fiber bundle are determined. Where, N is the total number of bundles of the carbon fiber bundles (1). Further, the proportion of carbon fiber bundles (1) relative to the total weight of carbon fiber bundles is determined by the following equation:

$$M_1/(M_1 + M_2) \times 100$$

(2) Flow test (stamping molding):

[0071] After two sheets of carbon fiber composite materials each having a size of 100 mm x 100 mm x 2 mm were preheated at a temperature of a melting point of a thermoplastic resin + 40°C (for example, 260°C in case of nylon 6), two sheets were stacked and placed on a press table heated at 120°C, and pressed at 20 MPa for 5 seconds. The area of the sheet after this pressing A2 and the area before the pressing A1 were measured, and A2/A1 was determined as flowability (%).

(3) Vf (content of carbon fibers in carbon fiber composite material):

[0072] A sample of about 2g was cut out from a molded article of a carbon fiber composite material, and the mass thereof was determined. Thereafter, the sample was heated in an electric furnace heated at 500°C for one hour and organic substances such as a matrix resin were burnt off. After cooled down to a room temperature, the mass of the residual carbon fibers was determined. The rate of the mass of the carbon fibers to the mass of the sample before being burnt off with organic substances such as a matrix resin was determined, and it was defined as the content of carbon fibers.

(4) Flexural test:

[0073] A flexural strength was determined based on JIS-K7171.

(5) Fiber strength utilization factor:

[0074] It was calculated by the following equation.
[0075] Fiber strength utilization factor = Flexural strength/Vf

(6) Single fiber flexural stiffness ($Pa \cdot m^4$):

[0076] It was calculated by Single fiber flexural stiffness = E x I.

Here, E: single fiber elastic modulus, and
I: geometrical moment of inertia.

[0077] The cross section of a fiber was supposed as a true circle, the geometrical moment of inertia was determined from the fiber diameter D, and the flexural stiffness was determined from the single fiber tensile elastic modulus and the geometrical moment of inertia.

(7) Drape value/single fiber flexural stiffness:

[0078] It was determined as an index of the convergence of a sizing agent (Sz agent) by dividing the drape value, that is an index representing the hardness of the carbon fiber bundle, with the single fiber flexural stiffness.

(8) Drape value (cm) of carbon fiber bundle:

[0079] As shown in Fig. 3(A), a carbon fiber bundle 21 drawn out from a bobbin without applying a tension is cut at a length of 40 cm, one end thereof is fixed by a fixing tape 22, a weight 23 of 100g is hung at the other end thereof, and after the twist and the bending are corrected, it is left in a measurement-temperature atmosphere for 30 minutes. Next, the weight 23 is removed, as shown in Fig. 3(B), the carbon fiber bundle 25 is placed on a horizontal and rectangular table 24 having a corner of 90° so as to protrude from the table by 25 cm, and after the part of carbon fibers on the table is fixed by a fixing tape 26 while the carbon fiber bundle with 40 cm is supported so as not to be broken, the support for the part protruding from the table is removed and the part is hung down, and after 2 seconds, the length of a horizontal distance L from the beginning point is measured, and the average value of "n" number of 3 times is defined as a drape value.

(9) Coefficient of friction:

[0080] A friction device was used wherein 5 stainless rods each having a diameter of 10 mm (chrome plating, surface roughness: 1 to 1.5s) were arranged in parallel to each other at an interval of 50 mm at a zigzag arrangement style so that a carbon fiber yarn could pass through the surfaces of the rods with a contact angle of 120° per each rod surface. The carbon fiber yarn was passed through this device at a yarn speed of 3 m/min. and an inlet side tension of 0.09g per

1 denier, and the coefficient of friction was determined from the rate of the inlet side tension and an outlet side tension by the following equation.

$$\text{Coefficient of friction} = (3/8\pi)\ln(T_2/T_1)$$

T_1: inlet side yarn tension
T_2: outlet side yarn tension

Examples

[0081] First, carbon fiber bundles and sizing agents used in Examples 1 to 7 and Comparative Examples 1 to 3 of the present invention will be explained.

[Carbon fiber bundle (A)]:

[0082] To a continuous carbon fiber bundle having a fiber diameter of 7 μm, a tensile elastic modulus of 230 GPa, a single fiber flexural stiffness of 2.71 x 10^{-11} Pa· m^4 and a number of filaments of 24,000, a sizing agent, prepared by preparing a mother liquor of the sizing agent by diluting glycerol triglycidyl ether with dimethyl formamide (hereinafter, abbreviated as DMF) so that the resin component became 1 wt.%, was provided to the carbon fibers by dipping method, and drying was carried out at 230°C. The adhesion amount was 0.4 wt.%.

[Carbon fiber bundle (B)]:

[0083] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A) other than a condition where the sizing agent was changed to glycerol diglycidyl ether.

[Carbon fiber bundle (C)]:

[0084] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A) other than a condition where the sizing agent was changed to polyethylene glycol diglycidyl ether (in the chemical formula [I], R^1 is $-CH_2CH_2-$ and m = 9).

[Carbon fiber bundle (D)]:

[0085] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A) other than a condition where the sizing agent was changed to diglycerol polyglycidyl ether.

[Carbon fiber bundle (E)]:

[0086] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A) other than a condition where the sizing agent was changed to diethylene glycol diglycidyl ether.

[Carbon fiber bundle (F)]

[0087] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A) other than a condition where the sizing agent was changed to bisphenol A type diglycidyl ether having an aromatic ring; "Epikote" 828 (epoxy compound having an aromatic ring) supplied by Yuka Shell Epoxy Kabushiki Kaisha.

[Carbon fiber bundle (G)]

[0088] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A) other than a condition where the sizing agent was changed to phenol novolak type glycidyl ether; "Epikote" 154 (epoxy compound having an aromatic ring) supplied by Yuka Shell Epoxy Kabushiki Kaisha.

Example 1:

[0089] The carbon fiber bundle (A) was cut at a fiber length of 15 mm, the cut carbon fiber bundles (A) and nylon 6 short fibers (fineness of short fiber: 1.7 dtex, cut length: 51 mm, number of crimps: 12 crests per 25 mm, rate of crimp: 15%) were mixed at a mass ratio of 90:10, and the mixture was introduced into a carding machine. The web having come out was cross wrapped to form a sheet-like carbon fiber nonwoven fabric comprising carbon fiber bundles (A) and nylon 6 fibers and having an areal weight of 100 g/cm^2. The proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 18 wt.%, the number average x of carbon fibers forming the bundle was 160, and the standard deviation σ was 70.

[0090] The winding direction of the sheet-like carbon fiber nonwoven fabric was referred to as 0°, the sheets of the carbon fiber nonwoven fabrics were stacked at 0°/90°, and further, after a nylon resin film ("CM1001", ηr = 2.3, supplied by Toray Industries, Inc.) was stacked so that the volume ratio of the carbon fibers to the thermoplastic resin became 30:70 as the whole of the stacked carbon fiber nonwoven fabrics, the whole was nipped by stainless plates, and after preheating at 260°C for 90 seconds, it was hot pressed at 260°C for 180 seconds while being applied with a pressure of 2.0 MPa. Then, it was cooled down to 50°C at the pressed condition to obtain a flat plate of carbon fiber composite material having a thickness of 2 mm. When the flexural strengths in 0° and 90° directions were determined relative to the 0° direction of the surface layer of the obtained flat plate, the average value of the flexural strengths in 0° and 90° directions was 485 MPa, the fiber strength utilization factor was 16.2 MPa/%, and the CV value was less than 5%.

[0091] When a sample having a size of 100 mm x 100 mm was cut out from the obtained flat plate and the flow test was performed, a good article could be obtained in which the flowability in the flow test was 270%. The conditions and the results of the determinations and the evaluations are shown in Table 1.

Example 2:

[0092] Example 2 was performed in a manner similar to that of Example 1 other than the conditions where a carbon fiber nonwoven fabric was formed in which the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 40 wt.%, the number average x of carbon fibers forming the bundle was 320, and the standard deviation σ was 200. When the flexural strengths in 0° and 90° directions and the flowability of the obtained flat plate were determined, a good article could be obtained in which the average value of the flexural strengths in 0° and 90° directions was 480 MPa, the fiber strength utilization factor was 16.0 MPa/%, the CV value was less than 5%, and the flowability was 290%.

Example 3:

[0093] Example 3 was performed in a manner similar to that of Example 1 other than the conditions where a carbon fiber nonwoven fabric was formed in which the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 62 wt.%, the number average x of carbon fibers forming the bundle was 615, and the standard deviation σ was 320. When the flexural strengths in 0° and 90° directions and the flowability of the obtained flat plate were determined, a good article could be obtained in which the average value of the flexural strengths in 0° and 90° directions was 463 MPa, the fiber strength utilization factor was 15.4 MPa/%, the CV value was less than 5%, and the flowability was 313%.

Examples 4-7, Comparative Examples 1-2:

[0094] Flat plates comprising carbon fiber nonwoven fabrics were obtained in a manner similar to that of Example 2 other than the conditions where the carbon fiber bundle (A) was changed to the carbon fiber bundle (B), (C), (D), (E), (F) or (G) as compared with Example 2. The conditions and the results of the determinations and the evaluations are shown together in Tables 1 and 2.

Comparative Example 3:

[0095] Comparative Example 3 was performed in a manner similar to that of Example 1 other than the conditions where a carbon fiber nonwoven fabric was formed in which the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 84 wt.%, the number average x of carbon fibers forming the bundle was 1,100, and the standard deviation σ was 630. When the flexural strengths in 0° and 90° directions and the flowability of the obtained flat plate were determined, the average value of the flexural strengths in 0° and 90° directions was 300 MPa, the fiber strength utilization factor was 10.0 MPa/%, the CV value was not less than 5%, and the flowability was 320%, and although the flowability was excellent, the flexural strength and the fiber strength utilization

factor were low, the mechanical properties were poor and the variability thereof was great.
[Table 1]

Table 1

Example		1	2	3	4	5	6	7
Carbon fiber bundle used before cutting		(A)	(A)	(A)	(B)	(C)	(D)	(E)
Carbon fiber cut length	[mm]	15	15	15	15	15	15	15
Proportion of carbon fiber bundles (1)	[%]	18	40	62	40	40	40	40
x : average value of number of fibers bundle	[number]	180	320	615	320	320	320	320
σ: standard deviation		107	200	320	200	200	200	200
Resin		CM1001	CM1001	CM1001	CM1001	CM1001	CM1001	CM1001
Vf	[%]	30	30	30	30	30	30	30
Flowability	[%]	270	290	313	293	291	300	293
Flexural strength (JIS-K7171)	[MPa]	485	480	463	484	487	473	486
CV value		○	○	○	○	○	○	○
Fiber strength utilization factor	[MPa/%]	16.2	16.0	15.4	16.1	16.2	15.8	16.2
○ :CV value is lower than 5%. × :C:V value is 5% or higher. [Table 2]								

Table 2

Comparative Example		1	2	3
Carbon fiber bundle used before cutting		(F)	(G)	(A)
Carbon fiber cut length	[mm]	15	15	15
Proportion of carbon fiber bundles (1)	[%]	39	41	84
x: average value of number of fibers forming bundle	[number]	314	330	1100
σ: standard deviation		197	220	630
Resin		CM1001	CM1001	CM1001
Vf	[%]	30	30	30
Flowability	[%]	280	288	320
Flexural strength (JIS-K7171)	[MPa]	421	417	310
CV value		○	○	×
Fiber strength utilization factor	[MPa/%]	14.0	13.9	10.3
○: CV value is lower than 5%. ×: CV value is 5% or higher.				

[0096] Next, carbon fibers and sizing agents used in Examples 8 to 14 and Comparative Examples 4 to 6 of the present invention will be explained.

[Carbon fiber bundle (A1)]:

[0097] To a continuous carbon fiber bundle having a fiber diameter of 7 μm, a tensile elastic modulus of 230 GPa, a single fiber flexural stiffness of 2.71 x 10^{-11} Pa· m^4 and a number of filaments of 24,000, a sizing agent, prepared by setting R^2 in the aforementioned chemical formula [I] to -CH_2CH_2-, R^3 to -CH_3, m to 2 and n to 2 and preparing a water emulsion in which the resin component of the sizing agent was 1 wt.%, was provided to the carbon fibers by dipping method, and drying was carried out at 180°C. The adhesion amount was 0.8 wt.%.

[Carbon fiber bundle (B1)]:

[0098] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A1) other than a condition where the sizing agent was changed to a sizing agent prepared by setting R^2 in the aforementioned chemical formula [I] to -CH_2CH_2-, R^3 to -CH_3, m to 5 and n to 5.

[Carbon fiber bundle (C1)]:

[0099] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A1) other than a condition where the sizing agent was changed to a sizing agent prepared by setting R^2 in the aforementioned chemical formula [I] to -CH_2CH_2-, R^3 to -CH_3, m to 10 and n to 10.

[Carbon fiber bundle (D1)]:

[0100] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A1) other than a condition where the sizing agent was changed to a sizing agent prepared by setting R^2 in the aforementioned chemical formula [I] to -CH_2CH_2-, R^3 to -H, m to 15 and n to 15.

[Carbon fiber bundle (E1)]:

[0101] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A1) other than a condition where the sizing agent was changed to a sizing agent prepared by setting R^2 in the aforementioned chemical formula [I] to -CH_2CH_2-, R^3 to -CH_3, m to 30 and n to 30.

[Carbon fiber bundle (F1)]

[0102] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A1) other than a condition where the sizing agent was changed to a sizing agent prepared by setting R^2 in the aforementioned chemical formula [I] to -OH, R^3 to - CH_3, m to 15 and n to 15.

[Carbon fiber bundle (G1)]

[0103] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A1) other than a condition where the sizing agent was changed to a sizing agent prepared by setting R^2 in the aforementioned chemical formula [I] to -CH_2CH_2-, R^3 to -CH_3, m to 1 and n to 1.

Example 8:

[0104] The carbon fiber bundle (A1) was cut at a fiber length of 15 mm, the cut carbon fiber bundles (A1) and nylon 6 short fibers (fineness of short fiber: 1.7 dtex, cut length: 51 mm, number of crimps: 12 crests per 25 mm, rate of crimp: 15%) were mixed at a mass ratio of 90:10, and the mixture was introduced into a carding machine. The web having come out was cross wrapped to form a sheet-like carbon fiber nonwoven fabric comprising carbon fiber bundles (A1) and nylon 6 fibers and having an areal weight of 100 g/cm^2. The proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 18 wt.%, the number average x of carbon fibers forming the bundle was 160, and the standard deviation σ was 70.

[0105] The winding direction of the sheet-like carbon fiber nonwoven fabric was referred to as 0°, the sheets of the carbon fiber nonwoven fabrics were stacked at 0°/90°, and further, after a nylon resin film ("CM1001", ηr = 2.3, supplied

by Toray Industries, Inc.) was stacked so that the volume ratio of the carbon fibers to the thermoplastic resin became 30:70 as the whole of the stacked carbon fiber nonwoven fabrics, the whole was nipped by stainless plates, and after preheating at 260°C for 90 seconds, it was hot pressed at 260°C for 180 seconds while being applied with a pressure of 2.0 MPa. Then, it was cooled down to 50°C at the pressed condition to obtain a flat plate of carbon fiber composite material having a thickness of 2 mm. When the flexural strengths in 0° and 90° directions were determined relative to the 0° direction of the surface layer of the obtained flat plate, the average value of the flexural strengths in 0° and 90° directions was 467 MPa, the fiber strength utilization factor was 15.6 MPa/%, and the CV value was less than 5%.

[0106] When a sample having a size of 100 mm x 100 mm was cut out from the obtained flat plate and the flow test was performed, a good article could be obtained in which the flowability in the flow test was 275%. The conditions and the results of the determinations and the evaluations are shown in Table 3.

Example 9:

[0107] Example 9 was performed in a manner similar to that of Example 8 other than the conditions where a carbon fiber nonwoven fabric was formed in which the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 40 wt.%, the number average x of carbon fibers forming the bundle was 320, and the standard deviation σ was 200. When the flexural strengths in 0° and 90° directions and the flowability of the obtained flat plate were determined, a good article could be obtained in which the average value of the flexural strengths in 0° and 90° directions was 461 MPa, the fiber strength utilization factor was 15.4 MPa/%, the CV value was less than 5%, and the flowability was 297%.

Example 10:

[0108] Example 10 was performed in a manner similar to that of Example 8 other than the conditions where a carbon fiber nonwoven fabric was formed in which the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 62 wt.%, the number average x of carbon fibers forming the bundle was 615, and the standard deviation σ was 320. When the flexural strengths in 0° and 90° directions and the flowability of the obtained flat plate were determined, a good article could be obtained in which the average value of the flexural strengths in 0° and 90° directions was 449 MPa, the fiber strength utilization factor was 15.0 MPa/%, the CV value was less than 5%, and the flowability was 318%.

Examples 11-14, Comparative Examples 4-5:

[0109] Flat plates comprising carbon fiber nonwoven fabrics were obtained in a manner similar to that of Example 9 other than the conditions where the carbon fiber bundle (A1) was changed to the carbon fiber bundle (B1), (C1), (D1), (E1), (F1) or (G1) as compared with Example 9 as shown in Tables 3 and 4. The conditions and the results of the determinations and the evaluations are shown together in Tables 3 and 4.

Comparative Example 6:

[0110] Comparative Example 6 was performed in a manner similar to that of Example 8 other than the conditions where a carbon fiber nonwoven fabric was formed in which the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers in the carbon fiber nonwoven fabric was 84 wt.%, the number average x of carbon fibers forming the bundle was 1,100, and the standard deviation σ was 630. When the flexural strengths in 0° and 90° directions and the flowability of the obtained flat plate were determined, the average value of the flexural strengths in 0° and 90° directions was 300 MPa, the fiber strength utilization factor was 10.0 MPa/%, the CV value was not less than 5%, and the flowability was 332%, and although the flowability was excellent, the flexural strength and the fiber strength utilization factor were low, the mechanical properties were poor and the variability thereof was great.

[Table 3]

Table 3

Example		8	9	10	11	12	13	14
Carbon fiber bundle used before cutting		(A1)	(A1)	(A1)	(B1)	(C1)	(D1)	(E1)

(continued)

Example		8	9	10	11	12	13	14
Number of atoms of epoxy / aromatic ring		8	8	8	17	32	47	92
Carbon fiber cut length	[mm]	15	15	15	15	15	15	15
Proportion of carbon fiber bundles (1)	[%]	18	40	62	40	40	40	40
x: average value of number of fibers forming bundle	[number]	180	320	615	320	320	320	320
σ: standard deviation		107	200	320	200	200	200	200
Resin		CM1001	CM1001	CM1001	CM1001	CM1001	CM1001	CM1001
Vf	[%]	30	30	30	30	30	30	30
Flowability	[%]	275	297	318	304	295	297	300
Flexural strength (JIS-K7171)	[MPa]	467	461	449	464	472	469	467
CV value		○	○	○	○	○	○	○
Fiber strength utilization factor	[MPa/%]	15.6	15.4	15.0	15.5	15.7	15.6	15.6
○: CV value is lower than 5%. ×: CV value is 5% or higher. [Table 4]								

Table 4

Comparative Example		4	5	6
carbon fiber bundle used before cutting		(F1)	(G1)	(A1)
Number of atoms of epoxy / aromatic ring		-	5	8
Carbon fiber cut length	[mm]	15	15	15
Proportion of carbon fiber bundles (1)	[%]	39	41	84
x: average value of number of fibers forming bundle	[number]	314	330	1100
σ: standard deviation		197	220	630
Resin		CM1001	CM1001	CM1001
Vf	[%]	30	30	30
Flowability	[%]	275	295	332
Flexural strength (JIS-K7171)	[MPa]	416	411	300
CV Value		○	○	×
Fiber strength utilization factor	[MPa/%]	13.9	13.7	10.0
○: CV value is lower than 5%. ×: CV value is 5% or higher.				

[0111] Next, carbon fibers and sizing agents used in Examples 15 to 26 and Comparative Examples 7 to 9 of the present invention will be explained.

[Carbon fiber bundle (A2)]:

[0112] As a sizing agent, a water dispersion emulsion having a concentration of 1 wt.% of a derivative of bisphenol A ethylene oxide adduct, set in the formula [III] of the aforementioned chemical formula 3 at R_1 = OH, R_2 = H, m = 15 and n = 15, was prepared. After a continuous carbon fiber bundle having a fiber diameter of 7 μm, a tensile elastic modulus of 230 GPa, a single fiber flexural stiffness of 2.71 x 10^{-11} Pa· m^4 and a number of filaments of 24,000 was dipped in this sizing agent emulsion through dip rollers, it was dried at 150°C for 1 minute using a hot air circulation type drier. When the adhesion amount of the sizing agent, the coefficient of friction and the drape value were determined, the adhesion amount was 0.8 wt.%, the coefficient of friction was 0.22 and the drape value was 5.3 cm.

[Carbon fiber bundle (B2)]:

[0113] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A2) with respect to the used carbon fibers and the method for providing a sizing agent, other than a condition where a water dispersion emulsion having a concentration of 1 wt.% of a compound, set in the formula [III] of the aforementioned chemical formula 3 at R_1 : a compound shown as the formula [VII] of the aforementioned chemical formula 7, R_2 = H, m = 15 and n = 15, was prepared as the sizing agent. When the adhesion amount of the sizing agent, the coefficient of friction and the drape value were determined, the adhesion amount was 0.9 wt.%, the coefficient of friction was 0.23 and the drape value was 5.5 cm.

[Carbon fiber bundle (C2)]:

[0114] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A2) with respect to the used carbon fibers and the method for providing a sizing agent, other than a condition where a water dispersion emulsion having a concentration of 1 wt.% of a compound, set in the formula [IV] of the aforementioned chemical formula 4 at R_1 = H, R_2 = OH, m = 10 and n = 10, was prepared as the sizing agent. When the adhesion amount of the sizing agent, the coefficient of friction and the drape value were determined, the adhesion amount was 0.6 wt.%, the coefficient of friction was 0.21 and the drape value was 5.0 cm.

[Carbon fiber bundle (D2)]:

[0115] 87g of anisotropic object mixture of 2· 4-/2· 6-tolylene diisocyanate and 34.4g of N-methyl dimethanol benzyl ammonium chloride were added to 260g of polypropylene glycol having a hydroxyl value of 112, and it was reacted in a nitrogen atmosphere at 40°C for 2 hours to prepare an urethane compound containing 2.23 wt.% of isocyanate group and 0.513 wt.% of quaternary nitrogen. To this, 41.3g of glycerol diglycidyl ether and 335.4g of DMF (dimethyl formamide) were added, it was reacted at 50°C for about 3 hours until the isocyanate group vanished. The reaction product was one containing 0.743g of oxirane oxygen and 0.476g of quaternary nitrogen and exhibiting a good water dispersion property.

[0116] To the above-described polyurethane obtained, dimethyl formamide solution containing 30 wt.% of bisphenol A diglycidyl ether type liquid epoxy resin having an epoxy equivalent of 225 to 280 and an average molecular weight of about 470 ("Epikote" 843, supplied by Shell Chemicals Ltd.) was added at a rate of 4:1, then, water was added and an emulsion of 1 wt.% thereof was prepared as a sizing agent. The other conditions were similar to those for the carbon fiber bundle (A2). When the adhesion amount of the sizing agent, the coefficient of friction and the drape value were determined, the adhesion amount was 0.8 wt.%, the coefficient of friction was 0.34 and the drape value was 10.5 cm.

[Carbon fiber bundle (E2)]:

[0117] The carbon fiber bundle was prepared in a manner similar to that in the carbon fiber bundle (A2) with respect to the used carbon fibers and the method for providing a sizing agent, other than a condition where a water dispersion emulsion having a concentration of 1 wt.% of a compound, set in the formula [III] of the aforementioned chemical formula 3 at R_1 = OH, R_2 = H, m = 1 and n = 1, was prepared as the sizing agent. When the adhesion amount of the sizing agent, the coefficient of friction and the drape value were determined, the adhesion amount was 0.7 wt.%, the coefficient of friction was 0.35 and the drape value was 6.2 cm.

Example 15:

[0118] The carbon fiber bundle (A2) was cut at a fiber length of 6 mm, the cut carbon fiber bundles and nylon 6 short fibers (fineness of short fiber: 1.7 dtex, cut length: 10 mm) were mixed at a mass ratio of 80:20, and the mixture was introduced into an air laid machine. The web having come out was heat treated to form a sheet-like carbon fiber nonwoven fabric comprising the carbon fibers and the nylon 6 fibers and having an areal weight of 200 g/cm^2. When the fiber bundles of the prepared nonwoven fabric were determined, the proportion of the carbon fiber bundles (1) relative to the total weight of carbon fibers was 13 wt.%, the number average x of carbon fibers forming the bundle was 160, and the standard deviation σ was 70.

[0119] The winding direction of the sheet-like carbon fiber aggregates was referred to as 0°, the sheets of the carbon fiber aggregates were stacked in a same direction, and after a nylon resin melt blow nonwoven fabric ("CM1001", ηr = 2.3, supplied by Toray Industries, Inc.) was stacked so that the volume ratio of the carbon fibers to the thermoplastic resin became 30:70 as the whole of the stacked carbon fiber aggregates, the whole was nipped by stainless plates, and after preheating at 260°C for 90 seconds, it was hot pressed at 250°C for 180 seconds while being applied with a pressure of 2.0 MPa. Then, it was cooled down to 50°C at the pressed condition to obtain a flat plate of carbon fiber composite material having a thickness of 2 mm. When the flexural strengths in 0° and 90° directions were determined relative to the 0° direction of the surface layer of the obtained flat plate, the average value of the flexural strengths in 0° and 90° directions was 470 MPa, the fiber strength utilization factor was 15.7 MPa/%, and the CV value was less than 5%.

[0120] When a sample having a size of 100 mm x 100 mm was cut out from the obtained flat plate and the flow test was performed, a good article could be obtained in which the flowability in the flow test was 300%. The conditions and the results of the determinations and the evaluations are shown in Table 5.

Examples 16-26:

[0121] Flat plates comprising carbon fiber nonwoven fabrics were obtained in a manner similar to that of Example 15 other than the conditions changed as compared with Example 15 as shown in Tables 5 and 6. The conditions and the results of the determinations and the evaluations are shown in Tables 5 and 6.

Comparative Example 7:

[0122] A Flat plate of a carbon fiber composite material comprising carbon fiber nonwoven fabrics was obtained in a manner similar to that of Example 15 other than the conditions where the carbon fiber bundle (D2) was cut at a fiber length of 15 mm, the cut carbon fiber bundles and nylon 6 discontinuous fibers (fineness of short fiber: 1.7 dtex, cut length: 10 mm) were mixed at a mass ratio of 80:20, and a carbon fiber nonwoven fabric was prepared in which the proportion of the carbon fiber bundles (1) was 23 wt.%, the number average x of carbon fibers forming the bundle was 250, and the standard deviation σ was 200. The conditions and the results of the determinations and the evaluations are shown in Table 7. The obtained carbon fiber nonwoven fabric is poor in flowability.

Comparative Example 8:

[0123] A Flat plate of a carbon fiber composite material comprising carbon fiber nonwoven fabrics was obtained in a manner similar to that of Example 15 other than the conditions where the carbon fiber bundle (E2) was cut at a fiber length of 15 mm, the cut carbon fiber bundles and nylon 6 discontinuous fibers (fineness of short fiber: 1.7 dtex, cut length: 10 mm) were mixed at a mass ratio of 80:20, and a carbon fiber nonwoven fabric was prepared in which the proportion of the carbon fiber bundles (1) was 22 wt.%, the number average x of carbon fibers forming the bundle was 260, and the standard deviation σ was 210. The conditions and the results of the determinations and the evaluations are shown together in Table 7. The obtained carbon fiber nonwoven fabric is poor in flowability.

Comparative Example 9:

[0124] A Flat plate of a carbon fiber composite material comprising carbon fiber nonwoven fabrics was obtained in a manner similar to that of Example 15 other than the conditions where the carbon fiber bundle (A2) was cut at a fiber length of 15 mm, the cut carbon fiber bundles and nylon 6 discontinuous fibers (fineness of short fiber: 1.7 dtex, cut length: 10 mm) were mixed at a mass ratio of 80:20, and a carbon fiber nonwoven fabric was prepared in which the proportion of the carbon fiber bundles (1) was 80 wt.%, the number average x of carbon fibers forming the bundle was 1,200, and the standard deviation σ was 630. The conditions and the results of the determinations and the evaluations are shown together in Table 7. Although the obtained carbon fiber nonwoven fabric is good in flowability, the fiber strength utilization factor is low and the variability in properties is great.

[Table 5]

Table 5

Example		15	16	17	18	19	20
Carbon fiber bundle used before cutting		(A2)	(A2)	(A2)	(A2)	(A2)	(A2)
Drape value / flexural stiffness	[cm/(Pa·cm^4)]	1.96×10^3	1.96×10^3	1.96×10^3	1.96×10^3	1.96×10^3	1.96×10^3
Carbon fiber cut length	[mm]	6	15	15	15	15	15
Proportion of carbon fiber bundles (1)	[%]	13	18	25	60	65	20
x: average value of number of fibers forming bundle	[number]	160	180	250	200	400	605
σ: standard deviation		70	87	130	130	190	320
Resin		CM1001	CM1001	CM1001	CM1001	CM1001	CM1001
Vf	[%]	30	30	30	30	30	30
Flowability	[%]	300	270	280	290	300	290
Flexural strength (JIS-K7171)	[MPa]	470	470	450	450	440	430
		○	○	○	○	○	○
Fiber strength utilization factor	[MPa/%]	15.7	15.7	15.0	15.0	14.7	14.3
○: CV value is lower than 5%. ×: CV value is 5% or higher. [Table 6]							

Table 6

Example		21	22	23	24	25	26
Carbon fiber bundle used before cutting		(A2)	(A2)	(A2)	(B2)	(B2)	(C2)
Drape value / flexural stiffness	[cm/(Pa·cm^4)]	1.96×10^3	1.96×10^3	1.96×10^3	2.03×10^3	2.03×10^3	1.84×10^3
Carbon fiber cut length	[mm]	15	15	15	15	15	15
Proportion of carbon fiber bundles (1)	[%]	26	72	80	60	66	64

(continued)

Example		21	22	23	24	25	26
x: average value of number of fibers forming bundle	[number]	840	550	860	200	405	395
σ: standard deviation		340	290	400	130	200	180
Resin		CM1001	CM1001	CM1001	CM1001	CM1001	CM1001
Vf	[%]	30	30	30	30	30	30
Flowability	[%]	300	320	320	300	305	300
Flexural strength (JIS-K7171)	[MPa]	410	410	390	470	460	450
CV value		○	○	○	○	○	○
fiber strength utilization factor	[MPa/%]	13.7	13.7	13.0	15.7	15.3	15.0
○: CV value is lower than 5%. ×: CV value is 5% or higher.							

[Table 7]

Table 7

Comparative Example		7	8	9
Carbon fiber bundle used before cutting		(D2)	(E2)	(A2)
Drape value /flexural stiffness	[cm/(Pa·cm^4)]	3.87×10^3	229×10^3	1.96×10^3
Carbon fiber cut length	[mm]	15	15	15
Proportion of carbon fiber bundles (1)	[%]	23	22	80
x: average value of number of fibers forming bundle	[number]	250	260	1200
σ: standard deviation		200	210	630
Resin		CM1001	CM1001	CM1001
Vf	[%]	30	30	30
Flowability	[%]	240	240	340
Flexural strength (JIS-K7171)	[MPa]	430	430	360
CV value		○	○	×
Fiber strength utilization factor	[MPa/%]	14.3	14.3	12.0
○: CV value is lower than 5%. ×: CV value is 5% or higher.				

Industrial Applicability

[0125] The carbon fiber nonwoven fabric according to the present invention can be applied to manufacture of any carbon fiber reinforced molded article required with both of high flowability and mechanical properties and small variability in mechanical properties , which has not been achieved by conventional technologies.

Explanation of symbols

[0126]

1: carding machine
2: cylinder roll
3: take-in roll
4: doffer roll
5: worker roll
6: stripper roll
7: feed roll
8: belt conveyer
9: discontinuous carbon fibers
10: sheet-like web
11: air laid machine
12: drum
13: pin cylinder
14: wire
15: suction box
21: carbon fiber bundle
22: fixing tape
23: weight
24: table
25: carbon fiber bundle
26: fixing tape

Claims

1. A carbon fiber nonwoven fabric including carbon fibers, **characterized in that** said carbon fibers are sized with an aliphatic compound having a plurality of epoxy groups, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000 fibers per bundle among carbon fiber bundles in said carbon fiber nonwoven fabric, and a standard deviation σ of the number of carbon fibers forming said carbon fiber bundle (1) is in a range of 50 to 500.

2. A carbon fiber nonwoven fabric including carbon fibers, **characterized in that** said carbon fibers are sized with an aromatic compound having a plurality of epoxy groups in which a number of atoms present between an epoxy group and an aromatic ring is 6 or more, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000 fibers per bundle among carbon fiber bundles in said carbon fiber nonwoven fabric, and a standard deviation σ of the number of carbon fibers forming said carbon fiber bundle (1) is in a range of 50 to 500.

3. The carbon fiber nonwoven fabric according to claim 1 or 2, wherein said compound having a plurality of epoxy groups is a compound having an epoxy group at each end of the longest atomic chain.

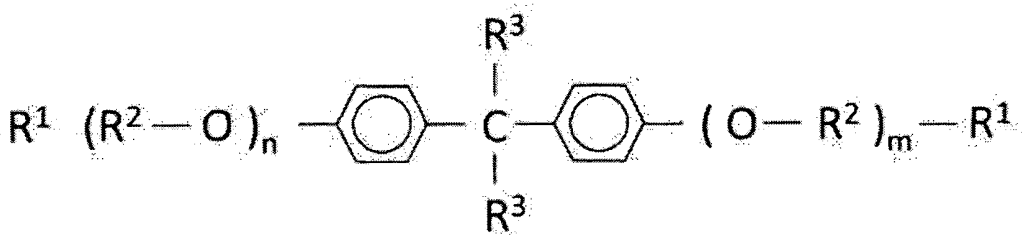
4. The carbon fiber nonwoven fabric according to claim 3, wherein said compound having a plurality of epoxy groups is a compound having an epoxy group only at each end of the longest atomic chain.

5. The carbon fiber nonwoven fabric according to claim 1 or 3, wherein a number of atoms of the longest atomic chain of said aliphatic compound having a plurality of epoxy groups is in a range of 20 to 200.

6. The carbon fiber nonwoven fabric according to any of claims 1 and 3 to 5, wherein said aliphatic compound having a plurality of epoxy groups is at least one kind of compound selected from glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyethylene glycol diglycidyl ether group and polypropylene glycol diglycidyl ether group.

7. The carbon fiber nonwoven fabric according to claim 2, wherein said aromatic compound having a plurality of epoxy groups in which a number of atoms present between an epoxy group and an aromatic ring is 6 or more is a compound shown in the following chemical formula 1.

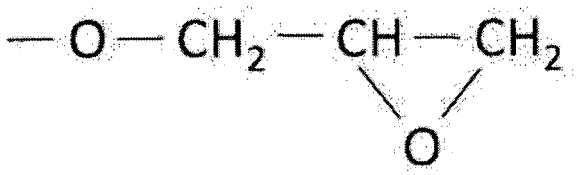
[Chemical formula 1]



[I]

(Where, R^1 in formula [I] is the following chemical formula 2,

[Chemical formula 2]



[II]

R^2 represents an alkylene group having a carbon number of 2 to 30, R^3 is -H or $-CH_3$, m and n represent an integer of 2 to 48, and m + n is in a range of 4 to 50.)

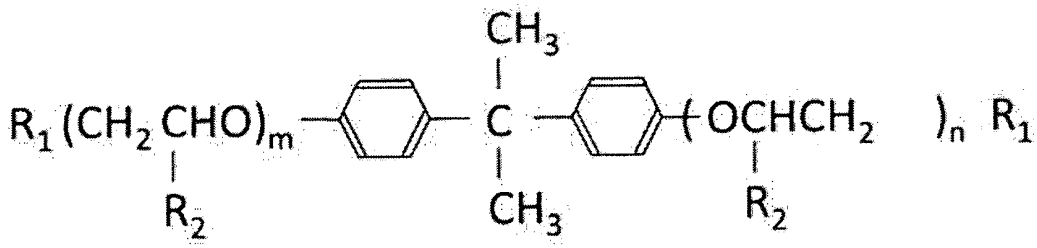
8. The carbon fiber nonwoven fabric according to claim 7, wherein said R^2 is $-CH_2CH_2-$ or $-CH(CH_3)\ CH_2-$.

9. The carbon fiber nonwoven fabric according to claim 2, wherein said aromatic compound is a condensed polycyclic aromatic compound.

10. The carbon fiber nonwoven fabric according to claim 9, wherein a skeletal structure of said condensed polycyclic aromatic compound is naphthalene, anthracene, phenanthrene or pyrene.

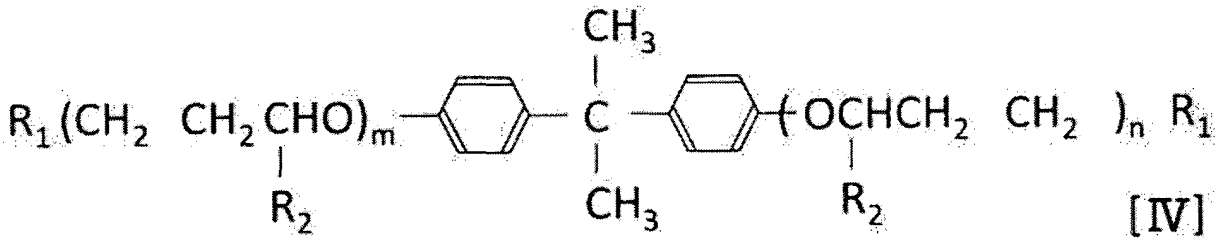
11. A carbon fiber nonwoven fabric including carbon fibers, **characterized in that** at least one kind of compound selected from chemical formulae (III), (IV) and (V) shown in the following chemical formula 3 to chemical formula 5 is made adhere to said carbon fibers at an amount of 0.1 to 5.0 wt.% relative to the weight of said carbon fibers of 100 wt.%, a number average x of carbon fibers forming a carbon fiber bundle (1), in which a number of carbon fibers forming a carbon fiber bundle is 90 or more, is in a range of 90 to 1,000 fibers per bundle among carbon fiber bundles in said carbon fiber nonwoven fabric, and a standard deviation σ of the number of carbon fibers forming said carbon fiber bundle (1) is in a range of 50 to 500.

[Chemical formula 3]



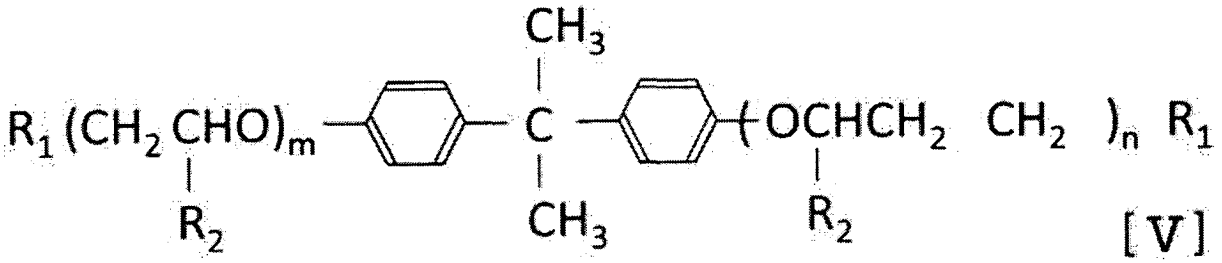
[III]

[Chemical formula 4]



[IV]

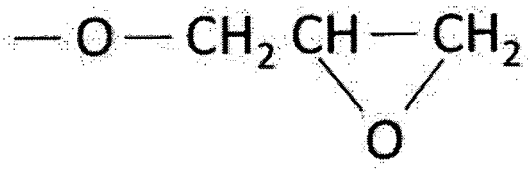
[Chemical formula 5]



[V]

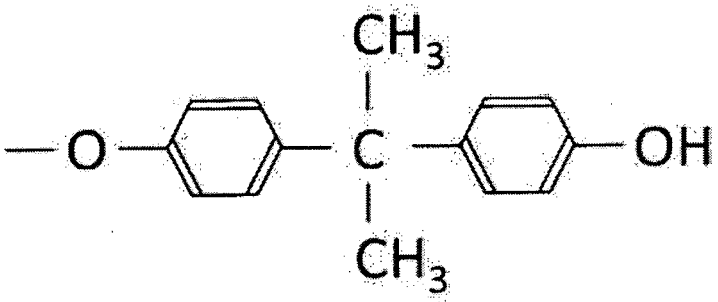
In the above-described formulae, R_1 represents H, OH, the following chemical formula 6 or the following chemical formula 7, R_2 represents H or OH, m and n represent an integer of 1 to 49, and m + n is in a range of 10 to 50.

[Chemical formula 6]



[VI]

[Chemical formula 7]



[VII]

12. The carbon fiber nonwoven fabric according to any of claims 1 to 11, wherein said standard deviation σ of the number of carbon fibers forming said carbon fiber bundle (1) is in a range of 50 to 350.

13. The carbon fiber nonwoven fabric according to any of claims 1 to 12, wherein a proportion of said carbon fiber bundles (1) relative to the total weight of carbon fibers is in a range of 5 to 80 wt.%.

14. The carbon fiber nonwoven fabric according to any of claims 1 to 13, wherein said carbon fiber nonwoven fabric is formed from a carbon fiber bundle whose drape value (cm)/single fiber flexural stiffness (Pa· cm^4) at 25°C is in a range of 1.4×10^3 to 4.0×10^3 (cm/(Pa· cm^4)).

15. The carbon fiber nonwoven fabric according to any of claims 1 to 14, wherein a single fiber flexural stiffness of carbon fibers forming said carbon fiber nonwoven fabric is in a range of 1.0×10^{-11} to 2.8×10^{-11} (Pa· cm^4).

16. The carbon fiber nonwoven fabric according to any of claims 1 to 15, wherein a fiber length Ln of carbon fibers forming said carbon fiber nonwoven fabric is in a range of 3 to 50 mm.

FIG. 1

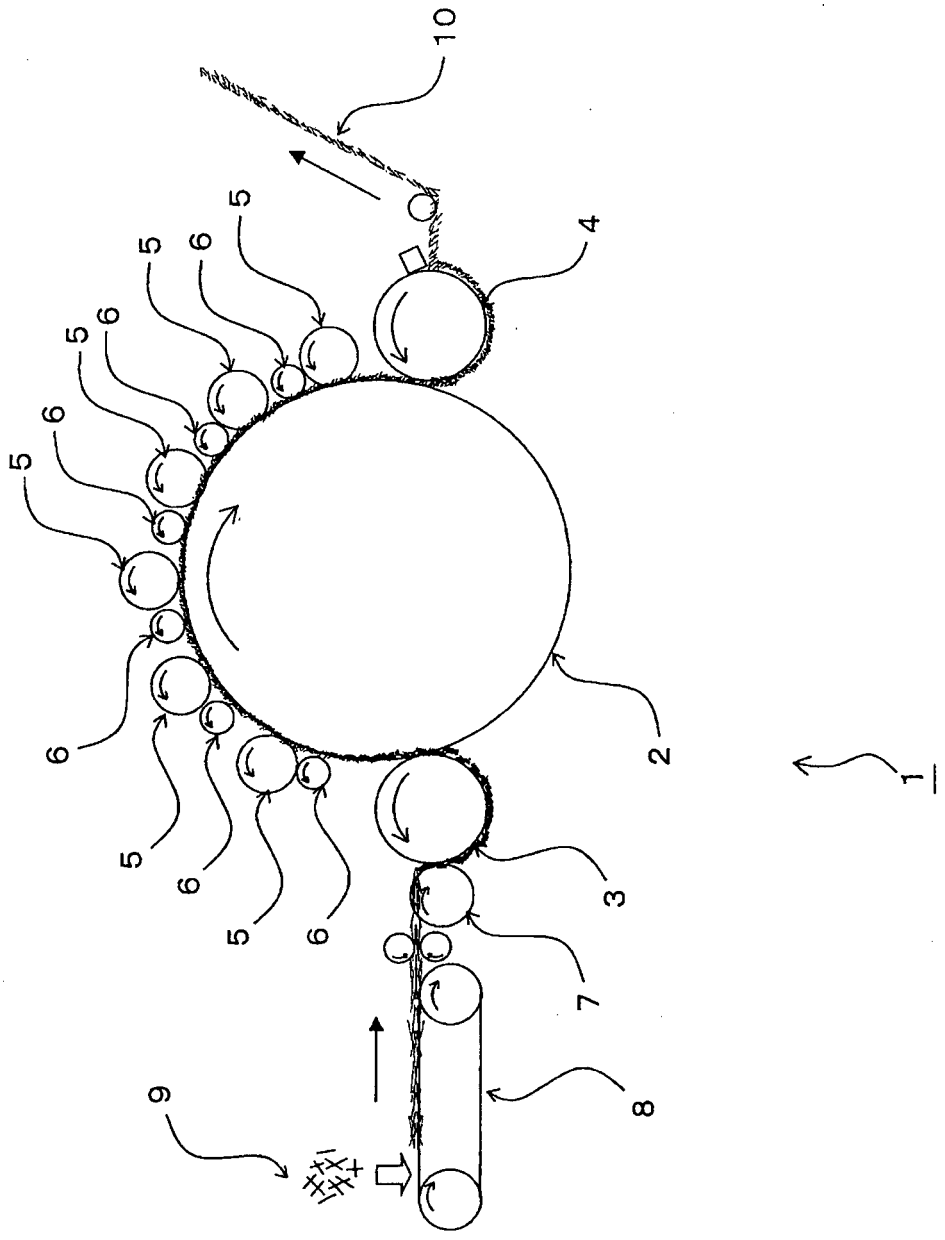


FIG. 2

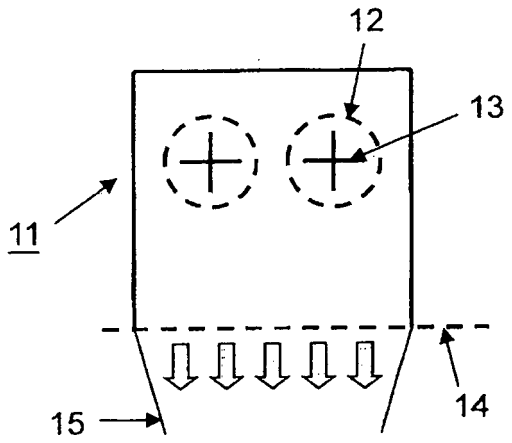
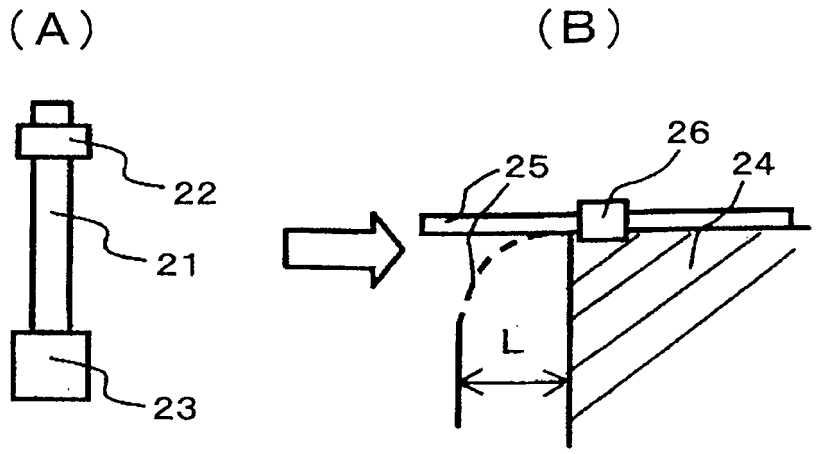


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/057105

A. CLASSIFICATION OF SUBJECT MATTER
D06M15/53(2006.01)i, *D04H1/4242*(2012.01)i, *D06M13/11*(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)
D06M13/00-15/715, D04H1/00-18/04, 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 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2012-158846 A (Teijin Ltd.), 23 August 2012 (23.08.2012), claims 1, 2, 6; paragraphs [0019], [0023], [0024]; example 2 (Family: none)	1-16
Y	JP 7-279040 A (Toray Industries, Inc.), 24 October 1995 (24.10.1995), claims; paragraphs [0015], [0176] & US 5462799 A claims; column 3, lines 11 to 15 & EP 640702 A1	1-10,12-16
Y	JP 7-9444 A (Toray Industries, Inc.), 13 January 1995 (13.01.1995), claims; paragraphs [0009], [0038] (Family: none)	11-16

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

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Date of the actual completion of the international search	Date of mailing of the international search report
29 May, 2014 (29.05.14)	10 June, 2014 (10.06.14)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/057105

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-264383 A (Toray Industries, Inc.), 29 September 2005 (29.09.2005), entire text (Family: none)	1-16
A	JP 2012-188770 A (Mitsubishi Rayon Co., Ltd.), 04 October 2012 (04.10.2012), entire text (Family: none)	1-16
A	JP 2011-214209 A (Toray Industries, Inc.), 27 October 2011 (27.10.2011), entire text (Family: none)	1-16
A	JP 2005-290614 A (Toho Tenax Co., Ltd.), 20 October 2005 (20.10.2005), entire text (Family: none)	1-16
A	JP 2011-157524 A (Toray Industries, Inc.), 18 August 2011 (18.08.2011), entire text (Family: none)	1-16
A	JP 2010-235779 A (Toray Industries, Inc.), 21 October 2010 (21.10.2010), entire text & US 2011/0143110 A1 & US 2012/0012263 A1 & EP 2314642 A1 & WO 2010/013645 A1 & CN 102056971 A & KR 10-2011-0055482 A & TW 201008988 A	1-16
P,X P,A	WO 2013/118689 A1 (Toray Industries, Inc.), 15 August 2013 (15.08.2013), paragraphs [0040], [0056]; examples; tables 1, 2 (Family: none)	1,3-6,11-16 2,7-10
P,X P,A	WO 2013/179891 A1 (Toray Industries, Inc.), 05 December 2013 (05.12.2013), entire text (Family: none)	1,3-6,11-16 2,7-10
P,X P,A	WO 2013/191073 A1 (Toray Industries, Inc.), 27 December 2013 (27.12.2013), entire text (Family: none)	1,3-6,11-16 2,7-10

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2012158846 A **[0005]**
- JP 2012158847 A **[0005]**