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(54) **Title:** SIZING AGENT FOR CARBON FIBER, CARBON FIBER, CARBON FIBER-REINFORCED COMPOSITE MATERIAL, AND METHOD OF PRODUCING CARBON FIBER-REINFORCED COMPOSITE MATERIAL

(57) **Abstract:** A sizing agent for carbon fiber includes a copolyamide dispersed in an aqueous medium and constituted by two or more monomer units selected from nylon 6, nylon 66, nylon 11, nylon 12, and nylon 610. The melting point of the copolyamide is 70 to 160°C. The melting point of the copolyamide when wet is 50 to 120°C.



SIZING AGENT FOR CARBON FIBER, CARBON FIBER, CARBON
FIBER-REINFORCED COMPOSITE MATERIAL, AND METHOD OF PRODUCING
CARBON FIBER-REINFORCED COMPOSITE MATERIAL

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates to a sizing agent for carbon fiber and to carbon fiber
obtained using this sizing agent for carbon fiber. The invention further relates to a
10 composite material that is reinforced and obtained using this carbon fiber and to a method
of producing this composite material.

2. Description of Related Art

[0002] Composite materials that use carbon fiber as a reinforcing fiber are light
15 weight and exhibit excellent mechanical properties, e.g., a high strength, and as a result
have in recent years come to be frequently used as components of, for example, aircraft
and automobiles. These composite materials are molded, for example, through molding
processing steps in which heat and pressure are applied, from prepregs, which are
intermediate products provided by impregnating the reinforcing fiber with a matrix resin.
20 This method, however, has problems with regard to process efficiency and also cannot be
applied to thermoplastic resins.

[0003] Reaction injection molding (RIM) is available as a method for producing
fiber-reinforced plastics. RIM is a molding method in which an unreacted liquid
precursor for the matrix resin, e.g., a polyamide (nylon), epoxy, urethane, and so forth, is
25 introduced into a mold in which the fibrous reinforcement is disposed and a reaction is
brought about and solidification is induced within the mold while the fibrous reinforcement
is impregnated with the liquid precursor. Polyurethanes, polyureas, polyamides, epoxies,
unsaturated polyesters, dicyclopentadiene, and so forth are used as matrix resins in RIM.
In polyamide RIM (nylon RIM), moldings are produced by the anionic polymerization of

ϵ -caprolactam. The catalyst used in polyamide RIM (nylon RIM) is an anionic catalyst that is a reaction product with, for example, an alkali metal, alkaline-earth metal, or Grignard reagent.

[0004] The efficient preparation of carbon fiber-reinforced thermoplastic resin moldings with excellent mechanical properties by RIM requires the preparation of a fabric (cloth) in which a high filament count carbon fiber tow is woven at high densities or the preparation of a nonwoven fabric with which a crimped thermoplastic fiber is blended and spun. It is also important that this cloth or nonwoven fabric not inhibit curing during the RIM process and that a removal step for moisture, which influences curing, can be omitted.

[0005] A sizing agent is typically applied during the production process in the case of commercially available carbon fiber tows and their plain weave cloths. This sizing agent has the effects of improving the gatherability or bundleability of the carbon fiber tow and improving the handling properties and abrasion resistance. The main purpose for applying this sizing agent is to avoid the occurrence of problems during the production process. As a consequence, most have reactive groups in the sizing agent that would inhibit curing and thus cannot be used as reinforcing fiber materials in RIM.

[0006] These sizing agents are required to have conflicting effects, i.e., an ability to improve the processability by weakly causing the fibers to adhere to each other and maintaining a condition in which the fibers are inhibited from separating from one another, and an ability to provide excellent wetting between the fibers and the matrix resin and thereby improve bonding at their interface. The sizing agents for the carbon fibers used as reinforcing fibers in FRPs can be exemplified by those based on water-soluble epoxy resins and those based on polyamide resins.

[0007] In the case of the epoxy resin sizing agents, their epoxy group reacts with the catalyst in the precursor for polyamide RIM. As consequence, catalyst required for the polyamide polymerization is deactivated by the epoxy resin sizing agent, resulting in a deficiency of the catalyst. Due to this, resin cure is inhibited, which causes a poor moldability and a reduction in properties.

[0008] In order to prevent this poor moldability and property reduction, Japanese

Patent Application Publication No. 10-286841 (JP 10-286841 A) provides for a reduction in the poor curability during RIM by a complete desizing of the epoxy sizing agent on the carbon fiber or by completely curing the epoxy groups in the sizing agent on the carbon fiber in order to extinguish these epoxy groups. However, due to poor adherence to the matrix resin, it has not been possible in either case to obtain a fiber-reinforced molding with the expected properties.

[0009] The polyamide resin sizing agents, on the other hand, do not deactivate the catalyst and thus are suitable for polyamide RIM; however, a drawback here has been that the sized carbon fiber has a hard yarn quality, resulting in a reduced weaving performance.

[0010] In order to resolve this drawback, a procedure is used in which the carbon fiber is sized using a water-soluble polyamide that has, for example, a polyethylene oxide structure, as proposed in Japanese Patent Application Publication Nos. 9-3777 (JP 9-3777 A) and 2002-88656 (JP 2002-88656 A). However, in both cases the water-soluble polyamide has a high saturated water absorption, which has caused concern with regard to deactivation of the curing agent during RIM.

SUMMARY OF THE INVENTION

[0011] The invention provides a RIM-adapted sizing agent for carbon fiber and provides carbon fiber that is obtained using this sizing agent. In addition, the invention provides carbon fiber-reinforced thermoplastic resin moldings that can be used, for example, for automotive parts.

[0012] The inventors carried out intensive investigations into a sizing agent for carbon fiber that would not produce the problems referenced above and that would not cause poor curing during RIM. As a result, they discovered that a sizing agent for carbon fiber that contains a particular copolyamide provides a RIM-adapted sizing agent that lacks the reactive groups and moisture that affect the curing agent during RIM. They additionally discovered that an improvement can also be brought about in the adherence between the matrix resin and, for example, a nonwoven fabric, fabric, or cut fiber of a carbon fiber tow that has been treated with this sizing agent.

[0013] A sizing agent for carbon fiber that is a first aspect of the invention includes a copolyamide dispersed in an aqueous medium and constituted by two or more monomer units selected from nylon 6, nylon 66, nylon 11, nylon 12, and nylon 610. The melting point of the copolyamide is 70 to 160°C. The melting point of the copolyamide when wet is 50 to 120°C.

[0014] The copolyamide in the first aspect of the invention may be constituted by at least one of a ternary copolyamide constituted by nylon 6, nylon 66, and nylon 12 monomer units and a quaternary copolyamide constituted by nylon 6, nylon 66, nylon 11, and nylon 12 monomer units.

[0015] In the first aspect of the invention, 70 to 10,000 weight parts of the aqueous medium may be contained per 100 weight parts of the copolyamide. In addition, the average particle diameter of a resin formed of the copolyamide may be 0.1 to 20 μm .

[0016] A second aspect of the invention is a carbon fiber. The sizing agent for carbon fiber according to the first aspect of the invention is attached to the carbon fiber that is the second aspect of the invention.

[0017] In the second aspect of the invention, the attachment rate of the sizing agent may be 0.3 to 20 weight% with respect to the carbon fiber.

[0018] The carbon fiber that is the second aspect of the invention may be a cut fiber, a nonwoven fabric with a crimped thermoplastic fiber, or an opened fabric.

[0019] A carbon fiber-reinforced composite material that is a third aspect of the invention is obtained by reaction injection molding of a polyamide resin and the carbon fiber that is the second aspect of the invention.

[0020] A fourth aspect of the invention is a method of producing a carbon fiber-reinforced composite material by mixing a polyamide resin and the carbon fiber that is the second aspect of the invention and reaction injection-molding the mixture.

[0021] A sizing agent for carbon fiber that is well adapted to RIM can be obtained according to the first aspect of the invention. In addition, the second through fourth aspects of the invention can stably provide a carbon fiber tow for molding that has been treated with this sizing agent, a nonwoven fabric with a crimped thermoplastic fiber, and a

well-opened carbon fiber fabric (cloth). Carbon fiber-reinforced thermoplastic resin moldings that can be used, for example, for automotive parts can also be provided.

DETAILED DESCRIPTION OF EMBODIMENTS

5 **[0022]** [The sizing agent for carbon fiber]

The sizing agent for carbon fiber according to the embodiments of the invention contains a copolyamide constituted by two or more monomer units selected from nylon 6, nylon 66, nylon 11, nylon 12, and nylon 610.

10 **[0023]** The copolyamide present in the sizing agent for carbon fiber according to the embodiments of the invention is an at least binary copolyamide that is constituted by at least two monomer units selected from nylon 6, nylon 66, nylon 11, nylon 12, and nylon 610. The copolyamide present in the sizing agent for carbon fiber according to the embodiments of the invention may be, for example, a binary copolyamide constituted by two monomer units, a ternary copolyamide constituted by three monomer units, or a
15 quaternary copolyamide constituted by 4 monomer units. The copolyamide present in the sizing agent for carbon fiber according to the embodiments of the invention is preferably a ternary copolyamide composed of the nylon 6, nylon 66, and nylon 12 monomer units; a quaternary copolyamide composed of the nylon 6, nylon 66, nylon 11, and nylon 12 monomer units; a ternary copolyamide composed of the nylon 6, nylon 12, and nylon 610
20 monomer units; a binary copolyamide composed of the nylon 6 and nylon 11 monomer units; or a binary copolyamide composed of the nylon 6 and nylon 12 monomer units. The copolyamide present in the sizing agent for carbon fiber according to the embodiments of the invention is more preferably a ternary copolyamide constituted by the nylon 6, nylon 66, and nylon 12 monomer units or a quaternary copolyamide constituted by the nylon 6,
25 nylon 66, nylon 11, and nylon 12 monomer units.

[0024] The copolyamide present in the sizing agent for carbon fiber according to the embodiments of the invention has a melting point of preferably 70 to 160°C, more preferably 100 to 155°C, and particularly preferably 120 to 150°C. This copolyamide can be adjusted to exhibit a desired melting point by changing the compositional proportions of

the copolymerization components.

[0025] As a general matter, in order to increase the adhesive strength the treatment temperature is desirably increased during the adhesion process; however, the adherend material may undergo degeneration or a decline in properties when it is subjected to a not insubstantial thermal history by the heat treatment applied during the adhesion process. As a consequence, a relatively lower melting point is desirable for the polymer that forms the adhesive component.

[0026] The melting point of the copolyamide in the sizing agent for carbon fiber according to the embodiments of the invention is therefore made not more than 160°C. Doing this makes it possible to lower the heat-treatment temperature during the adhesion process and to thereby reduce to a minimum the degeneration or property decline in the adherend material. A lower heat-treatment temperature during the adhesion process is also preferable in terms of energy consumption and cost.

[0027] When, on the other hand, the melting point of the copolyamide is less than 70°C and a high-temperature and high-humidity environment is encountered during storage or transport, the strands of the carbon fiber yarn may then melt-bond to each other, creating the risks of unreeling problems and a reduction in yarn quality. This is also unfavorable because the durability is then poor — for example, detachment may occur — when a heat treatment is carried out on the adherend material that has been subjected to the adhesion process.

[0028] The melting point of the copolyamide in the sizing agent for carbon fiber according to the embodiments of the invention was measured based on the method described in JIS K 7121 using a Thermo plus DSC 8230L differential scanning calorimeter from Rigaku Corporation at a temperature ramp rate of 10°C/minute.

[0029] The inhibition of curing by the epoxy group in the epoxy-based sizing agents used as sizing agents for carbon fiber is a cause of cure inhibition during RIM processes. Further, moisture exercises a substantial effect and as a consequence the sizing agent used must have a small saturated water absorption.

[0030] For example, in the case of use of a water-soluble polyamide having a

polyethylene oxide structure, its high saturated water absorption results in a high water solubility and facile use and processing. However, the use of a water-soluble polyamide having a polyethylene oxide structure causes the water-soluble polyamide resin coating to be hygroscopic and water absorptive with elapsed time post-attachment to the carbon fiber, and a large amount of moisture may thus be present during RIM as a result and the curing agent may then be deactivated during RIM.

[0031] As a result, it was realized that it would be favorable to use, as a sizing agent for carbon fiber, a copolyamide resin that had a saturated water absorption sufficiently low as to not cause cure inhibition during the RIM process.

[0032] The melting point of the copolyamide when wet according to the embodiments of the invention is preferably 50 to 120°C, more preferably 65 to 110°C, and particularly preferably 68 to 106°C. When the melting point when wet is in the indicated range, the copolyamide can then be readily dispersed in the aqueous medium.

[0033] When the copolyamide according to the embodiments of the invention is dispersed in the aqueous medium, the saturated water-absorption is formed at a temperature at or above the melting point of the copolyamide. Thus, a lower melting point for the copolyamide in the range from 70 to 160°C is preferred. However, while a lower melting point for the copolyamide is advantageous, when the melting point is less than 70°C the strands of the sized carbon fiber may then melt-bond to each other during carbon fiber storage or transport, creating the risk of unreeling problems and a reduction in yarn quality. On the other hand, the copolyamide may undergo degradation when the melting point is a temperature higher than 160°C.

[0034] In addition, since the copolyamide is dispersed in the aqueous medium under wet-heat conditions while heating, a lower melting point when wet can make dispersion of the copolyamide easier. Due to this, the melting point when wet is preferably not more than 120°C. Softening of the copolyamide in the aqueous medium occurs when the melting point when wet is a temperature less than 50°C and the dispersion of the copolyamide dispersed in the aqueous medium may then become unstable.

[0035] The melting point of the copolyamide when wet according to the

embodiments of the invention is measured by the following method. A fineness $\times 1/30$ g clip-form weight is attached at an end of the fiber-form (length = 30 cm) copolyamide according to the embodiments of the invention and the fiber-form copolyamide is hung in a water bath with a water temperature of 20°C, completely immersed over a length of 20 cm with the weight-attached end down. The water temperature is then raised at 12°C/minute and the fiber-form copolyamide is melted and the melting point when wet is taken to be the water temperature when the weight drops off.

[0036] Water is preferred for the aqueous medium used to disperse the copolyamide according to the embodiments of the invention, and various types of water can be used, for example, tap water, industrial water, ion-exchanged water, deionized water, and pure water. Deionized water and pure water are particularly preferred. As necessary, a pH modifier, viscosity modifier, fungicide, and so forth may be added as appropriate to this water within a range in which the objects of the invention are not impaired.

[0037] The amount of use of the water used to disperse the copolyamide according to the embodiments of the invention in the sizing agent for carbon fiber according to the embodiments of the invention, expressed per 100 weight parts of the copolyamide, is generally 70 to 10,000 weight parts and is preferably 90 to 10,000 weight parts. When the amount of water use is less than 70 weight parts, an adequate dispersion of the copolyamide in the water may not be possible; when used in excess of 10,000 weight parts, the resulting aqueous copolyamide dispersion will have a low concentration, which is disadvantageous from a use standpoint.

[0038] The average particle diameter of the copolyamide particles dispersed in the aqueous medium in the sizing agent for carbon fiber according to the embodiments of the invention is adjusted to 0.1 to 20 μm and preferably to 0.1 to 10 μm . When the average particle diameter of the copolyamide resin in the aqueous copolyamide dispersion is less than 0.1 μm , the particles are prone to aggregation and gelation and due to this it may be difficult to bring to a high resin concentration. When the average particle diameter of the copolyamide resin in the aqueous copolyamide dispersion exceeds 20 μm , problems occur with the uniformity of the coating layer and a decline in the adhesive

strength of the sizing agent is produced. In the embodiments of the invention, the average particle diameter is measured by a laser diffraction particle size distribution measurement method.

[0039] The sizing agent for carbon fiber according to the embodiments of the invention is obtained, for example, by preparing an aqueous dispersion of the copolyamide by dispersing the copolyamide in the aqueous medium.

[0040] The method for dispersing the copolyamide in the aqueous medium, while not being particularly limited, can be exemplified by methods in which shear force is applied by stirring with a stirring blade-equipped stirrer and methods in which melt kneading is performed using a twin-screw extruder.

[0041] A stable aqueous dispersion can be made in the aforementioned production methods when the terminal carboxyl groups of the copolyamide are treated with a basic substance and dispersion is carried out by applying a shear force by stirring at a temperature equal to or greater than the softening point of the copolyamide in an aqueous dispersion that as necessary contains a surfactant and/or a dispersing agent.

[0042] The basic substance can be exemplified by alkali metal hydroxides such as sodium hydroxide and potassium hydroxide and by ammonia and amine compounds. The use is particularly preferred from the standpoint of the dispersing effect of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

[0043] The surfactant can be exemplified by anionic surfactants, e.g., rosin acid salts, fatty acid salts, and alkylbenzenesulfonate salts; nonionic surfactants, e.g., ethylene oxide/propylene oxide block copolymers, polyoxyethylene alkyl ethers, glycerol/fatty acid esters, and polyoxyethylene fatty acid ethanolamides; and amphoteric surfactants.

[0044] The dispersing agent can be exemplified by polymeric dispersing agents such as polyacrylate salts, polystyrenesulfonate salts, the salts of styrene/maleic anhydride copolymers, polyvinyl alcohols, and hydroxyethyl cellulose, and by inorganic dispersing agents such as alumina sols, silica sols, and calcium phosphate.

[0045] [Carbon fiber to which the sizing agent is attached]

The embodiments of the invention also include carbon fiber to which the

above-described sizing agent for carbon fiber is attached. In the embodiments of the invention, "carbon fiber" includes both the individual carbon fibers and the carbon fiber tow that is their aggregate or bundle.

[0046] There are no particular limitations on the carbon fiber used and conventional carbon fibers can be used. Examples are polyacrylonitrile-based carbon fibers (PAN-based carbon fibers), rayon-based carbon fibers, lignin-based carbon fibers, pitch-based carbon fibers, vapor phase-grown carbon fibers, carbon nanotubes, and so forth, and there are no particular limitations on the species as long as it has a fibrous shape. A PAN-based carbon fiber is preferably used because this enables the realization of a low cost and because the carbon fiber-reinforced composite material obtained from the carbon fiber has excellent mechanical properties.

[0047] Carbon fiber having the sizing agent for carbon fiber according to the embodiments of the invention attached thereto is obtained by treating the carbon fiber with this sizing agent for carbon fiber and drying.

[0048] The sizing treatment may be a conventional sizing treatment that may be carried out using a sizing agent for carbon fiber that is an aqueous dispersion, but is not otherwise particularly limited, and can be exemplified by methods in which the carbon fiber is sized with the sizing agent by a common method, e.g., a dip method, spray method, or roller method. The drying method is not particularly limited and, for example, a method that uses a thermal medium, e.g., a hot wind, hot plate, roller, or infrared heater, can be selected.

[0049] When carbon fiber sized with the sizing agent for carbon fiber according to the embodiments of the invention is woven while applying heat, processing by opening the carbon fiber tow can be carried out relatively easily; however, the processability may be reduced when the amount of sizing agent attachment on the carbon fiber is raised. Since the fiber is itself brittle, the bundleability of the carbon fiber used in RIM must be raised and it must be handled as the tow.

[0050] Accordingly, in those instances in which a high filament count carbon fiber tow is used and priority is given to the openability (spreadability) and weaveability,

the amount of sizing agent attachment must be reduced to preferably not more than 2 weight% and more preferably to 1 weight%. When, on the other hand, little sizing agent is present on the carbon fiber, the fibers adhere weakly to one another and readily separate from one another and, for example, napping is prone to appear and the processability may be reduced. In addition, the effect of providing an excellent wettability between the fiber and matrix resin and thereby improving the adherence at their interface cannot be realized.

[0051] In the embodiments of the invention, therefore, the sizing treatment is preferably carried out using a method in which a plain weave fabric of carbon fiber, or a nonwoven fabric of carbon fiber and a crimped thermoplastic fiber, is continuously sized, possibly with the implementation of a desizing step depending on the circumstances.

[0052] The prescribed sizing agent can be uniformly attached in this method by attaching the sizing agent by roll coating while immersing the plain weave carbon fiber fabric or carbon fiber/crimped thermoplastic fiber nonwoven fabric in a sizing bath; controlling the amount of sizing agent attachment by adjusting the nip roller pressure with, for example, an adjustable mangle; carrying out continuous drying; and winding up.

[0053] The amount of attachment of the sizing agent (but excluding the aqueous medium) for carbon fiber according to the embodiments of the invention, while not being particularly limited, is preferably 20 weight% to 0.3 weight% and more preferably 10 weight% to 0.5 weight%, expressed with respect to the carbon fiber before treatment. The properties of the copolyamide itself do not affect the properties of the molding when the amount of sizing agent attachment is not more than 20 weight%. A satisfactory bundleability can be imparted to the carbon fiber when the amount of sizing agent attachment is at least 0.3 weight%.

[0054] The sizing agent for carbon fiber according to the embodiments of the invention is preferably used by itself, and sizing is carried out with this sizing agent using an ordinary method, for example, a dipping method, spraying method, or roller method. The sized carbon fiber is dried at from at least 100°C to not more than 250°C. Controlling the attachment rate of the copolyamide resin here into the range from 20 weight% to 0.3 weight% is preferred from the standpoint of the hardness of the carbon

fiber and the problem of curing agent deactivation during RIM curing.

[0055] In order to increase the properties of the molding yielded by RIM, the carbon fiber according to the embodiments of the invention is preferably a high filament count carbon fiber tow and in specific terms has a filament count of preferably at least 15,000 and more preferably at least 45,000. The upper limit on this filament count is preferably at most 100,000 and more preferably is 70,000 or less and should be selected considering the spreadability.

[0056] The carbon fiber tow for molding according to the embodiments of the invention is not limited to RIM applications, and, for example, molding may also be carried out by converting this carbon fiber tow for molding into a cut fiber and mixing this into a molding resin followed by introduction into a mold. A 3 to 20 mm cut fiber is preferably used in such cases.

[0057] The carbon fiber tow according to the embodiments of the invention may also contain, within a range in which the objects of the invention are not impaired, small amounts of other types of fibers. These other types of fibers can be exemplified by high-strength, high-modulus fibers such as glass fiber, aramid fiber, alumina fiber, silicon carbide fiber, boron fiber, and metal fiber, and one or more of these may be incorporated.

[0058] [The carbon fiber-reinforced composite material]

The embodiments of the invention also relate to a carbon fiber-reinforced composite material obtained by RIM of a matrix resin and a carbon fiber (including carbon fiber tow) that has been treated with the sizing agent for carbon fiber according to the embodiments of the invention. The embodiments of the invention in particular relate to a carbon fiber-reinforced composite material obtained by RIM of a polyamide resin and a carbon fiber that has been treated with the sizing agent for carbon fiber according to the embodiments of the invention. A carbon fiber-reinforced composite material can be produced — without causing the inhibition of resin cure due to the reaction of the sizing agent with the catalyst in the RIM precursor — when RIM is carried out using a polyamide resin as the matrix resin and a carbon fiber that has been treated with the sizing agent for carbon fiber according to the embodiments of the invention.

[0059] The matrix resin can be selected in the embodiments of the invention from thermosetting resins and thermoplastic resins. Thermoplastic resins, which enable injection molding and press molding at high molding efficiencies and high mechanical properties for the resulting carbon fiber-reinforced composite material, are preferred.

5 [0060] The thermoplastic resins can be exemplified by polyesters (for example, polyethylene terephthalate and polybutylene terephthalate), polyolefins (for example, polyethylene, polypropylene, and polybutylene), styrenic resins, polyoxymethylene, polyamide, polycarbonate, polymethyl methacrylate, polyvinyl chloride, polyphenylene sulfide, polyphenylene ether, polyimide, polyamideimide, polyetherimide, polysulfone, 10 polyethersulfone, polyketone, polyetherketone, polyetheretherketone, polyarylate, polyethernitrile, phenol phenoxy resins, and fluororesins. The thermoplastic resins may also be exemplified by thermoplastic elastomers such as polystyrene types, polyolefin types, polyurethane types, saturated polyester types, polyamide types, polybutadiene types, polyisoprene types, and fluorine types. Polyamide resins, which can provide carbon 15 fiber-reinforced composite materials with excellent mechanical properties, are preferably used as the thermoplastic resin. Also usable as the thermoplastic resin are copolymers of the preceding, modifications of the preceding, and blends of two or more of the preceding. These modifications refer to derivatives obtained by substituting a reactive functional group, e.g., the carboxyl group, within the molecular structure and derivatives provided by 20 the addition of a diol, e.g., the oxyethylene group, within the molecular structure.

[0061] The carbon fiber-reinforced composite material according to the embodiments of the invention can be obtained, for example, by mixing the matrix resin and a carbon fiber (including carbon fiber tow) that has been treated with the sizing agent for carbon fiber according to the embodiments of the invention and injection molding this 25 mixture in a mold. The mixing proportions are not particularly limited, but, for example, the amount of the carbon fiber that has been treated with the sizing agent for carbon fiber according to the embodiments of the invention, expressed per 100 weight parts of the matrix resin, is preferably 2.5 to 1,000 weight parts and more preferably 5 to 300 weight parts. The matrix resin and the sizing agent for carbon fiber according to the

embodiments of the invention may be mixed using a conventional method capable of mixing them to uniformity. For example, mixing of the matrix resin with the sizing agent for carbon fiber according to the embodiments of the invention may be carried out according to an ordinary method using a conventional apparatus, e.g., a single-screw extruder, twin-screw extruder, press machine, high-speed mixer, injection molder, or pultrusion molder. Depending on, for example, its composition and blending method, the mixture may be obtained in various forms, such as a particulate mixture of the matrix resin and carbon fiber, a granulate made from this mixture, and so forth. Other conventional additives may as necessary also be combined in this mixture. These additives can be specifically exemplified by antioxidants, thermal stabilizers, weathering inhibitors, release agents, lubricants, pigments, dyes, plasticizers, static inhibitors, flame retardants, reinforcing materials, and so forth.

[0062] The sizing agent for carbon fiber according to the embodiments of the invention can provide, via RIM using a polyamide resin as the matrix resin, a carbon fiber-reinforced composite material with excellent mechanical properties, e.g., flexural strength and flexural modulus, and can do so without causing an inhibition of resin cure.

[0063] The invention is described in additional detail through the examples provided below, but the invention is not particularly limited to or by the examples.

[0064] (The copolyamide sizing agent for carbon fiber)

Example 1 of the invention is described in the following. 150 kg of a ternary copolyamide resin constituted by the nylon 6, nylon 66, and nylon 12 monomer units (product name: H005FA, melting point = approximately 120°C, melting point when wet = 72°C, from Arkema, Inc.), 149.6 kg water, and 0.4 kg sodium hydroxide were introduced into a jacketed pressure-resistant autoclave having an internal volume of 450 L, an internal diameter of 700 mm, and a height of 1500 mm and equipped with a turbine-type stirring blade with a diameter of 350 mm and the autoclave was sealed. The stirrer was then started and the temperature in the autoclave interior was raised to around 150°C while stirring at 150 rpm. After stirring for an additional 30 minutes while holding the internal temperature at 140 to 150°C, the contents were cooled to 50°C to yield the aqueous

copolyamide resin dispersion (sizing agent for carbon fiber) of Example 1 having a resin concentration of 50 weight%. The median diameter of the obtained copolyamide resin sizing agent for carbon fiber, as measured using a laser diffraction particle size distribution analyzer (LA-910 from Horiba, Ltd.), was 1.6 μm .

5 **[0065]** Example 2 of the invention is described in the following. 40 kg of a quaternary copolyamide constituted by the nylon 6, nylon 66, nylon 11, and nylon 12 monomer units (product name: M2468, melting point = 105°C, melting point when wet = 68°C, from Arkema, Inc.) was introduced from the upstream side of a twin-screw extruder (S-4KRC from Kurimoto, Ltd.) and was melt-kneaded at a cylinder temperature of 140°C and a rotation rate of 450 rpm. After melt-kneading, 16 kg of a 0.9 weight% aqueous sodium hydroxide solution was fed from a feed port.

15 **[0066]** The set conditions were changed to a cylinder temperature of 100°C and a rotation rate of 450 rpm and 44 kg of pure water was gradually added from a feed port on the twin-screw extruder and kneading was carried out, followed by passage through a die element (die temperature = 100°C) and discharge from the twin-screw extruder. By opening a switching valve, 1 L of the aqueous polyamide resin dispersion was introduced into a stirred tank having an internal volume of 2 L and equipped with a propeller-type stirrer. The liquid temperature immediately after introduction was 95°C as measured with a temperature sensor. Then, while stirring, cooling was continued until the liquid temperature reached 35°C. Stirring was stopped at the same time that 35°C was reached and cooling was carried out to room temperature (25°C) to obtain the aqueous polyamide resin dispersion of Example 2 (sizing agent for carbon fiber) (effective concentration = 40%), which had a median diameter of 1.2 μm .

25 **[0067]** Example 3 of the invention is described in the following. The aqueous copolyamide resin dispersion (sizing agent for carbon fiber) of Example 3, which had a resin concentration of 50 weight%, was obtained proceeding as in Example 1, but in this case changing the ternary copolyamide resin constituted by the nylon 6, nylon 66, and nylon 12 monomer units (product name: H005FA, melting point = approximately 120°C, melting point when wet = 72°C, from Arkema, Inc.) to a ternary copolyamide constituted

by the nylon 6, nylon 12, and nylon 610 monomer units (product name: DAIAMID, melting point = approximately 130°C, melting point when wet = 90°C, from Daicel-Evonik Ltd.).

[0068] Example 4 of the invention is described in the following. The aqueous
5 copolyamide resin dispersion (sizing agent for carbon fiber) of Example 4, which had a resin concentration of 50 weight%, was obtained proceeding as in Example 1, but in this case changing the ternary copolyamide resin constituted by the nylon 6, nylon 66, and nylon 12 monomer units (product name: H005FA, melting point = approximately 120°C, melting point when wet = 72°C, from Arkema, Inc.) to a binary copolyamide constituted
10 by the nylon 6 and nylon 11 monomer units (product name: M995, melting point = approximately 150°C, melting point when wet = 106°C, from Arkema, Inc.).

[0069] Example 5 of the invention is described in the following. The aqueous
copolyamide resin dispersion (sizing agent for carbon fiber) of Example 5, which had a resin concentration of 50 weight%, was obtained proceeding as in Example 1, but in this
15 case changing the ternary copolyamide resin constituted by the nylon 6, nylon 66, and nylon 12 monomer units (product name: H005FA, melting point = approximately 120°C, melting point when wet = 72°C, from Arkema, Inc.) to a binary copolyamide constituted by the nylon 6 and nylon 12 monomer units (product name: M1186, melting point = approximately 140°C, melting point when wet = 93°C, from Arkema, Inc.).

20 [0070] Comparative Example 1 is described in the following. Stable aqueous dispersions, as obtained in Examples 1 to 5, could not be obtained in Comparative Example 1 for the aqueous dispersions of the individual nylons, i.e., nylon 6, nylon 66, nylon 11, nylon 12, and nylon 610, because all of these individual nylons had melting points of 170°C or more.

25 [0071] Comparative Example 2 is described in the following. A stable aqueous dispersion, as obtained in Examples 1 to 5, could not be obtained in Comparative Example 2 because the melting point of nylon 6/nylon 66 = 60/40, which has the lowest melting point of the binary copolyamides constituted by the nylon 6 and nylon 66 monomer units, was 180°C.

[0072] (Production of carbon fiber tow)

[Measurement of the amount of sizing agent attachment]

Approximately 2 g of the carbon fiber tow was dried for 30 minutes at 105°C, then cooled to room temperature over 30 minutes in a desiccator and weighed (W1).

5 Following this, the carbon fiber tow was immersed in acetone and the sizing agent was cleaned off. The cleaned sample was dried for 1 hour at 105°C, then cooled to room temperature over 30 minutes in a desiccator and weighed (W2). The amount of sizing agent attachment was determined using the following formula.

10
$$\text{amount of sizing agent attachment (weight\%)} = [W1 \text{ (g)} - W2 \text{ (g)}] / [W2 \text{ (g)}] \times 100$$

[0073] [Measurement of the saturated water absorption of the sizing agent]

In accordance with the method of JIS K 7209 A, the sizing agent was dried for 24 hours at 120°C and approximately 10 g of the dried resin was then accurately weighed (weight A); the accurately weighed dried resin was subsequently introduced into a water-filled container held at $23 \pm 2^\circ\text{C}$; and the dried resin was removed from the water after 24 ± 1 hours. The weight gain by the resin at this point (weight B) was accurately weighed, and the saturated water absorption of the sizing agent was calculated using the following formula.

20

$$\text{saturated water absorption (\%)} = 100 \times \text{weight B} / \text{weight A}$$

[0074] [Evaluation of RIM polymerization]

Test tube A: ϵ -caprolactam (15 g) and dicyclohexylcarbodiimide (0.55 g) were introduced into a test tube under a nitrogen atmosphere and 3 g of the carbon fiber tow prepared in the particular example or comparative example was also added. Test tube B: ϵ -caprolactam (15 g) and sodium hydride (0.07 g) were added to a separate test tube under a nitrogen atmosphere.

[0075] Test tube A and test tube B were heated for 20 minutes on a 200°C oil bath

and the ϵ -caprolactam was melted, and the contents of test tube A and test tube B were then mixed and a polymerization reaction was run at 150°C. Inhibition of the polymerization reaction was judged based on an evaluation of the degree to which the cure time was lengthened relative to the cure time for the system to which the completely uncoated carbon fiber tow was added.

[0076] [Criteria for evaluating the RIM polymerization]

The evaluation was carried out as follows: O (circle) was assigned when curing occurred in a cure time less than 1.1-times the cure time for the use of the carbon fiber tow to which there was no addition at all; Δ (triangle) was assigned when curing occurred in a cure time of 1.1- to 1.5-times the cure time for the use of the carbon fiber tow to which there was no addition at all; and $\times$ (cross) was assigned when curing occurred in a cure time equal to or greater than 1.5-times the cure time for the use of the carbon fiber tow to which there was no addition at all.

[0077] [Measurement of the flexural strength and flexural modulus of the fiber-reinforced moldings]

The flexural strength and flexural modulus of the fiber-reinforced moldings were measured based on JIS 7171.

[0078] The method of producing the carbon fiber tow of Example 6 of the invention is described in the following. A PAN-based carbon fiber strand with a filament diameter of 7 μm and a constituent filament count of 24,000 (Torayca T700SC from Toray Industries, Inc.) was subjected, while the strand was being continuously run, to a desizing step in a first step, a sizing step in a second step, and a drying step in a third step. A desized carbon fiber tow was first obtained by immersion with ceramic guides of the carbon fiber strand in a stirring apparatus-equipped acetone bath as a desizing bath, then re-immersion with ceramic guides in a stirring apparatus-equipped acetone bath, then immersion with ceramic guides in a water tank filled with ion-exchanged water, and removal of the excess moisture with a roller press. The resulting carbon fiber tow was sized by roll immersion in a sizing bath of the aqueous sizing agent dispersion with an effective concentration of 4 weight%. This sizing bath was adjusted by the addition of

ion-exchanged water to the copolyamide sizing agent for carbon fiber obtained according to Example 1. The amount of sizing agent attachment on the carbon fiber was adjusted to the prescribed amount using nip rollers. Drying was subsequently carried out by pressure contact for 150 seconds with a drying roller heated to 120°C, and a secondary drying was additionally performed for 100 seconds by impinging with air heated to 180°C. The amount of attachment of the sizing agent for the obtained carbon fiber tow of Example 6 was 1 weight%.

[0079] Production of the carbon fiber tows of Examples 7 and 8 of the invention was carried out proceeding as in Example 6, but bringing the amount of sizing agent attachment on the carbon fiber to 2 weight% and 3 weight%, respectively, by changing the effective concentration of the copolyamide sizing agent for carbon fiber.

[0080] Production of the carbon fiber tow of Example 9 of the invention was carried out proceeding as in Example 6, but using the sizing agent of Example 2 as the copolyamide sizing agent for carbon fiber and bringing the amount of sizing agent attachment on the carbon fiber to 10 weight% by changing the effective concentration of the sizing agent.

[0081] Production of the carbon fiber tow of Example 10 of the invention was carried out proceeding as in Example 6, but using the sizing agent of Example 3 as the copolyamide sizing agent for carbon fiber and bringing the amount of sizing agent attachment on the carbon fiber to 5 weight% by changing the effective concentration of the sizing agent.

[0082] Production of the carbon fiber tow of Example 11 of the invention was carried out proceeding as in Example 6, but using the sizing agent of Example 4 as the copolyamide sizing agent for carbon fiber and bringing the amount of sizing agent attachment on the carbon fiber to 5 weight% by changing the effective concentration of the sizing agent.

[0083] Production of the carbon fiber tow of Example 12 of the invention was carried out proceeding as in Example 6, but using the sizing agent of Example 5 as the copolyamide sizing agent for carbon fiber and bringing the amount of sizing agent

attachment on the carbon fiber to 5 weight% by changing the effective concentration of the sizing agent.

5 **[0084]** The production of the carbon fiber tow of Example 13 of the invention was carried out as follows. A sizing treatment was performed by roll immersion of a PAN-based carbon fiber strand with a filament diameter of 7 μm and a constituent filament count of 24,000 (Torayca T700SC from Toray Industries, Inc.) in a sizing bath of the aqueous sizing agent dispersion having an effective concentration of 4 weight%. This sizing bath was adjusted by the addition of ion-exchanged water to the copolyamide sizing agent for carbon fiber obtained according to Example 1. The amount of attachment of the sizing agent overcoated on the carbon fiber was controlled to the prescribed amount using nip rollers. Drying was subsequently carried out by pressure contact for 150 seconds with a drying roller heated to 120°C, and a secondary drying was performed for 100 seconds by impinging with air heated to 180°C. The amount of attachment of the sizing agent for the obtained carbon fiber tow was 1 weight%.

15 **[0085]** The production of the carbon fiber tows of Examples 14 and 15 of the invention was carried out proceeding as in Example 13, but changing the amount of sizing agent attachment on the carbon fiber to 2 weight% and 3 weight%, respectively, by changing the effective concentration of the copolyamide sizing agent for carbon fiber that was applied as an overcoating.

20 **[0086]** For the carbon fiber tow production method of Comparative Example 3, the RIM polymerization evaluation was run on the PAN-based carbon fiber strand (Torayca T700SC-24000 from Toray Industries, Inc.) without performing thereon any treatment at all.

25 **[0087]** In the carbon fiber tow production method of Comparative Example 4, the RIM polymerization evaluation was run after using a polyether-block-amide copolymer (Pebax MV1074 from Arkema, Inc.)(R-1) as the sizing agent.

[0088] In the carbon fiber tow production method of Comparative Example 5, the RIM polymerization evaluation was run after using a polyether-block-amide copolymer (Pebax MV3000 from Arkema, Inc.)(R-2) as the sizing agent.

[0089] The RIM polymerization evaluation was performed using the carbon fibers obtained in Examples 6 to 15 and Comparative Examples 3 to 5. The results are summarized in Table 1. Here, the amount of sizing agent attachment for Examples 13 to 15 represents the amount of attachment for the sizing agent applied as an overcoating. The published value was used for the amount of sizing agent attachment in Comparative Example 3. The "polymerization inhibition" in the table uses the criteria for evaluating RIM polymerization as described above. Thus, the "polymerization inhibition" indicates the evaluation of the cure time for the extent of polymerization inhibition, relative to the case in which nothing at all was applied to the carbon fiber tow.

[Table 1]

	sizing agent			saturated water ab- sorption (%)	desizing? yes/no	attachment rate (%)	polymerization inhibition
	type	melting point (°C)	melting point when wet (°C)				
Example 6	Example 1	120	72	2.0	yes	1	O
Example 7	Example 1	120	72	2.0	yes	2	O
Example 8	Example 1	120	72	2.0	yes	3	O
Example 9	Example 2	105	68	2.0	yes	10	O
Example 10	Example 3	130	90	3.5	yes	5	O
Example 11	Example 4	150	106	3.5	yes	5	O
Example 12	Example 5	140	93	3.0	yes	5	O
Example 13	Example 1	120	72	2.0	no	1	Δ
Example 14	Example 1	120	72	2.0	no	2	O - Δ
Example 15	Example 1	120	72	2.0	no	3	O
Comparative Example 3						1	×
Comparative Example 4	R-1			48.0	yes	1	×
Comparative Example 5	R-2			28.0	yes	1	×

[0090] As is clear from Table 1, the carbon fiber tows sized with the sizing agents of Examples 1 to 5 of the invention were shown to not cause cure inhibition (polymerization inhibition) in RIM using ϵ -caprolactam. In addition, the results for Examples 13 to 15 demonstrated the effectiveness of performing a re-sizing treatment after the carbon fiber tow had been desized.

[0091] [Production of a carbon fiber nonwoven fabric]

A carbon fiber nonwoven fabric according to Example 16 of the invention was produced as follows. A fiber blend was first prepared from 30 weight% nylon 6 short fiber (from Toray Industries, Inc., single fiber fineness = 1.7 dtex, cut length = 51 mm, crimp count = 12/25 mm, crimp ratio = 15%) and 70 weight% 50 mm chopped fiber from carbon fiber provided by desizing a carbon fiber (from Toray Industries, Inc., Torayca T700SC-24000, amount of attachment of epoxy resin-based sizing agent: 1.0 to 1.2 weight%). A nonwoven fabric (width = 110 cm, length = 30 m, areal weight = 250 g/m²) with an excellent longitudinal · transverse strength balance was obtained by processing the prepared blend through the individual steps of an opener, roller card, crosslayer, roller card, and needle punching. The obtained nonwoven fabric was immersed in a sizing bath of an aqueous sizing agent dispersion adjusted to an effective concentration of 3 weight%. This sizing bath was adjusted by the addition of ion-exchanged water to the copolyamide resin sizing agent obtained in Example 1. This was followed by roller coating and then adjustment of the amount of sizing agent attachment by adjusting the pressure (squeezing) of the nip rollers of a mangle. The obtained nonwoven fabric was continuously dried for 200 seconds at 120°C using a convection dryer while being spread out with a pin-type tenter and was wound up. The amount of sizing agent attachment for the obtained nonwoven fabric was 1 weight%.

[0092] The carbon fiber nonwoven fabrics of Examples 17 and 18 of the invention were produced proceeding as in Example 16, but bringing the amount of sizing agent attachment on the carbon fiber to 5 weight% and 10 weight%, respectively, by changing the effective concentration of the sizing agent.

[0093] The carbon fiber nonwoven fabric of Example 19 of the invention was produced proceeding as in Example 16, but using the sizing agent of Example 2 as the copolyamide sizing agent for carbon fiber and changing the effective concentration of the sizing agent to bring the amount of attachment of the sizing agent on the carbon fiber to 3 weight%.

[0094] The carbon fiber nonwoven fabric of Example 20 of the invention was produced proceeding as in Example 16, but using the sizing agent of Example 3 as the

copolyamide sizing agent for carbon fiber and changing the effective concentration of the sizing agent to bring the amount of attachment of the sizing agent on the carbon fiber to 15 weight%.

[0095] The carbon fiber nonwoven fabric of Example 21 of the invention was
5 produced proceeding as in Example 16, but using the sizing agent of Example 4 as the copolyamide sizing agent for carbon fiber and changing the effective concentration of the sizing agent to bring the amount of attachment of the sizing agent on the carbon fiber to 5 weight%.

[0096] The carbon fiber nonwoven fabric of Example 22 of the invention was
10 produced proceeding as in Example 16, but using the sizing agent of Example 5 as the copolyamide sizing agent for carbon fiber and changing the effective concentration of the sizing agent to bring the amount of attachment of the sizing agent on the carbon fiber to 5 weight%. The properties of these carbon fiber nonwoven fabrics are summarized in Table 2.

[0097] [Production of a carbon fiber-reinforced composite material by nylon
15 RIM]

A carbon fiber-reinforced composite material was produced by nylon RIM as follows. First, the mold was heated to the prescribed temperature and the interior of the mold was then brought to a -90 kPa reduced pressure from atmospheric pressure using a vacuum
20 pump. Then, a precursor A (ϵ -caprolactam + dicyclohexylcarbodiimide) and a precursor B (ϵ -caprolactam + sodium hydride) were heated to 110°C using a dryer and were melted. After melting, the precursor A and the precursor B were rapidly mixed to provide a monomer melt which, after the disposition within the mold of 8 stacked layers of the 160 × 160 mm carbon fiber nonwoven fabric obtained in Example 16, was injected into the
25 interior of the mold, which had been heated to 160°C, and molding was carried out. The properties of these moldings are summarized in Table 2.

[Table 2]

	sizing agent		properties of the moldings	
	type of sizing agent	amount of sizing agent (weight%)	flexural strength (MPa)	flexural modulus (GPa)
Example 16	Example 1	1	223.3	13.0
Example 17	Example 1	5	318.3	15.6
Example 18	Example 1	10	288.3	14.9
Example 19	Example 2	3	306.5	15.3
Example 20	Example 3	15	266.8	13.8
Example 21	Example 4	5	285.6	14.2
Example 22	Example 5	5	305.1	14.8
Comparative Example 6	—	0	196.0	11.6
Comparative Example 7			156.7	9.1
Comparative Example 8	R-1	5	151.2	8.8
Comparative Example 9	R-2	5	171.1	9.8

[0098] In the production method for the carbon fiber nonwoven fabric of

Comparative Example 6, a fiber blend was prepared from 30 weight% nylon 6 short fiber
 5 (from Toray Industries, Inc., single fiber fineness = 1.7 dtex, cut length = 51 mm, crimp
 count = 12/25 mm, crimp ratio = 15%) and 70 weight% 50 mm chopped fiber from carbon

fiber provided by desizing a carbon fiber (from Toray Industries, Inc., Torayca T700SC-24000, amount of attachment of epoxy resin-based sizing agent: 1.0 to 1.2 weight%). The evaluation was run using a nonwoven fabric with an excellent longitudinal · transverse strength balance and obtained by processing the prepared blend
5 through the individual steps of an opener, roller card, crosslayer, roller card, and needle punching.

[0099] The same RIM was performed using a nonwoven fabric obtained, in the production method for the carbon fiber nonwoven fabric of Comparative Example 7, from nylon 6 short fiber and chopped fiber from a carbon fiber that had been treated with an
10 epoxy resin-based sizing agent (Toray Industries, Inc., Torayca T700SC-24000). However, good-quality moldings could not be obtained, due to a moisture-induced cure inhibition

[0100] The same RIM was performed with the production method for the carbon fiber nonwoven fabric of Comparative Example 8, which used a polyether-block-amide
15 copolymer (Pebax MV1074 from Arkema, Inc.) for the sizing agent (R-1). The same RIM was also run with the production method for the carbon fiber nonwoven fabric of Comparative Example 9, which used a polyether-block-amide copolymer (Pebax MV3000 from Arkema, Inc.) for the sizing agent (R-2). However, good-quality moldings could not
20 be obtained, due to a moisture-induced cure inhibition, with the methods for producing the carbon fiber nonwoven fabrics of Comparative Examples 8 and 9.

[0101] Table 2 shows that the nonwoven fabric obtained from sized carbon fiber could provide moldings with better properties than nonwoven fabric obtained from unsized carbon fiber. In addition, based on the results for Examples 16 to 22 and Comparative
25 Examples 8 and 9, the nonwoven fabrics sized with the sizing agents of Examples 1 to 5 gave better results than the nonwoven fabrics sized with an epoxy-based sizing agent or a water-soluble polyamide.

[0102] [Production of a carbon fiber plain weave fabric (cloth)]

The production of the carbon fiber plain weave fabric of Example 23 was carried out as follows. A carbon fiber plain weave fabric (Toho Tenax Co., Ltd.: W3101) that had

been desized with solvent acetone was immersed in a sizing bath of the aqueous sizing agent dispersion adjusted to a 5 weight% effective concentration. The sizing bath was adjusted by the addition of ion-exchanged water to the copolyamide resin sizing agent obtained in Example 1. Roller coating was performed on the plain weave fabric that had
5 been immersed in the sizing bath, and the amount of sizing agent attachment was then adjusted by adjusting the pressure (squeezing) of the nip rollers of a mangle. The obtained plain weave fabric was continuously dried for 200 seconds at 120°C using a convection dryer while being spread out with a pin-type tenter and was wound up. The amount of sizing agent attachment for the obtained plain weave fabric was 1 weight%.

10 **[0103]** Production of the carbon fiber plain weave fabrics of Examples 24 and 25 was carried out proceeding as in Example 23, but changing the amount of sizing agent attachment for the carbon fiber plain weave fabrics to 5 weight% and 10 weight%, respectively, by changing the effective concentration of the sizing agent. Their properties are summarized in Table 3.

15 **[0104]** Production of the carbon fiber plain weave fabrics of Examples 26 to 29 was carried out proceeding as in Example 24, but changing the sizing agent from the sizing agent of Example 1 to the sizing agents of Examples 2 to 5, respectively. Their properties are summarized in Table 3.

20 **[0105]** [Production of a carbon fiber-reinforced composite material by nylon RIM]

A carbon fiber-reinforced composite material was produced by nylon RIM as follows. First, the mold was heated to the prescribed temperature and the interior of the mold was then brought to a -90 kPa reduced pressure from atmospheric pressure using a vacuum pump. Then, a precursor A (ϵ -caprolactam + dicyclohexylcarbodiimide) and a precursor
25 B (ϵ -caprolactam + sodium hydride) were heated to 110°C using a dryer and were melted. After melting, the precursor A and the precursor B were rapidly mixed to provide a monomer melt which, after the disposition within the mold of 8 stacked layers of the 160 × 160 mm carbon fiber cloth obtained in Example 23, was injected into the interior of the mold, which had been heated to 160°C, and molding was carried out. The properties of

these moldings are summarized in Table 3.

[Table 3]

	sizing agent		properties of the moldings	
	type of sizing agent	amount of sizing agent (weight%)	flexural strength (MPa)	flexural modulus (GPa)
Example 23	Example 1	1	465.7	40.0
Example 24	Example 1	5	486.7	45.6
Example 25	Example 1	10	408.6	41.6
Example 26	Example 2	5	477.6	40.9
Example 27	Example 3	5	416.8	38.6
Example 28	Example 4	5	412.3	42.8
Example 29	Example 5	5	402.2	41.5
Comparative Example 10	—	0	187.7	25.8
Comparative Example 11			165.0	23.7
Comparative Example 12	R-1	5	78.9	16.1
Comparative Example 13	R-2	5	90.6	17.8

[0106] In the production method for the carbon fiber plain weave fabric of

5 Comparative Example 10, the evaluation was carried out using a carbon fiber plain weave fabric (Toho Tenax Co., Ltd.: W3101) that had been desized as the reinforcing fiber fabric

without re-sizing.

[0107] In the production method for the carbon fiber plain weave fabric of Comparative Example 11, the evaluation was carried out using a carbon fiber plain weave fabric (Toho Tenax Co., Ltd.: W3101) on which no treatment at all had been performed.

5 [0108] The carbon fiber plain weave fabrics of Comparative Examples 12 and 13 were produced proceeding as in Example 24, but changing the sizing agent from the sizing agent of Example 1 to, respectively, a polyether-block-amide copolymer (Pebax MV1074 from Arkema, Inc.) as the sizing agent (R-1) and a polyether-block-amide copolymer (Pebax MV3000 from Arkema, Inc.) as the sizing agent (R-2).

10 [0109] Table 3 shows that well-opened plane weave fabrics sized with the copolyamide can provide moldings that have excellent properties and can do so without the occurrence of curing defects during RIM.

CLAIMS:

1. A sizing agent for carbon fiber, comprising
a copolyamide dispersed in an aqueous medium and constituted by two or more monomer units selected from nylon 6, nylon 66, nylon 11, nylon 12, and nylon 610, wherein
a melting point of the copolyamide is 70 to 160°C, and
a melting point of the copolyamide when wet is 50 to 120°C.
2. The sizing agent for carbon fiber according to claim 1, wherein
the copolyamide is constituted by at least one of a ternary copolyamide constituted by nylon 6, nylon 66, and nylon 12 monomer units and a quaternary copolyamide constituted by nylon 6, nylon 66, nylon 11, and nylon 12 monomer units.
3. The sizing agent for carbon fiber according to claim 1 or 2, wherein
70 to 10,000 weight parts of the aqueous medium is contained per 100 weight parts of the copolyamide, and
an average particle diameter of a resin formed of the copolyamide is 0.1 to 20 μm .
4. A carbon fiber characterized in that
the sizing agent according to any one of claims 1 to 3 has been attached to the carbon fiber.
5. The carbon fiber according to claim 4, wherein
an attachment rate of the sizing agent is 0.3 to 20 weight% with respect to the carbon fiber.
6. The carbon fiber according to claim 4 or 5, wherein
the carbon fiber is a cut fiber, a nonwoven fabric with a crimped thermoplastic fiber,

or an opened fabric.

7. A carbon fiber-reinforced composite material characterized in that the carbon fiber-reinforced composite material is obtained by reaction injection molding of a polyamide resin and the carbon fiber according to any one of claims 4 to 6.

8. A method of producing a carbon fiber-reinforced composite material, comprising:
mixing a polyamide resin and the carbon fiber according to any one of claims 4 to 6;
and
reaction injection-molding the mixture.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/001955

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06M15/59 C08J5/06
ADD.

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)
D06M C08J C08G

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/133421 A1 (TEIJIN LTD [JP]) 12 September 2013 (2013-09-12) abstract & EP 2 824 235 A1 (TEIJIN LTD [JP]) 14 January 2015 (2015-01-14) abstract examples	1-8
X	JP 2013 104156 A (SUMITOMO SEIKA CHEMICALS) 30 May 2013 (2013-05-30) abstract paragraph [0012] - paragraph [0013] paragraph [0030] examples 1-3 ----- -/--	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/001955

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2013 087396 A (SUMITOMO SEIKA CHEMICALS) 13 May 2013 (2013-05-13) abstract paragraph [0010] paragraph [0039] examples	1-8
X	----- JP H07 299875 A (SUMITOMO RUBBER IND) 14 November 1995 (1995-11-14) abstract paragraph [0033] examples	1-8
X,P	----- WO 2013/172318 A1 (TEIJIN LTD [JP]) 21 November 2013 (2013-11-21) examples	1-6
X,P	----- WO 2014/136888 A1 (SUMITOMO SEIKA CHEMICALS [JP]) 12 September 2014 (2014-09-12) examples -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

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