Abstract:

EPOXY RESIN COMPOSITION, PREPREG, AND FIBER REINFORCED PLASTIC MATERIAL

The embodiments herein relate to an epoxy resin composition comprising at least one naphthalene-based epoxy resin containing at least two naphthalene moieties and at least one glycidyl ether group per molecule, a prepreg, and a fiber-reinforced composite material. More specifically, the embodiments herein relate to an epoxy resin composition containing a combination of particular types of epoxy resin and curatives that provides high flexural modulus and low water absorption and that is suitable for preparing a fiber-reinforced composite material capable of withstanding extreme use environments. In addition, the embodiments herein relate to epoxy resin systems capable of achieving a high degree of cure (e.g., 90% or more) within a relatively short period of time (e.g., two hours) at a relatively low temperature (e.g., 132°C).
EPOXY RESIN COMPOSITION, PREPREG, AND FIBER
REINFORCED PLASTIC MATERIAL

Cross-Reference to Related Applications

This application claims priority to United States Provisional Application Nos. 62/312,668, filed 24 March 2016, and 62/455,219, filed 6 February 2017. The disclosure of each of these applications is incorporated herein by reference in its entirety for all purposes.

Field of the Invention

The present application provides an epoxy resin composition for fiber-reinforced composite materials that are well-suited for aerospace applications, sports applications, and general industrial applications.

Background of the Invention

Fiber Reinforced Plastic (FRP) materials consisting of a reinforced fiber and a matrix resin have excellent mechanical properties such as strength and rigidity while being lightweight, and therefore are widely used as aircraft members, spacecraft members, automobile members, railway car members, ship members, sports apparatus members, and electronic members such as computer housings for laptops. Typically, reinforcement fibers are in the form of woven cloth or continuous filaments. These FRP materials can be produced using filament winding methods, prepreg laminating methods, molding methods, pultrusion methods, or the like, but the prepreg laminating method is predominantly used to obtain high-performance FRP materials. Prepreg laminating is a method in which a prepreg or prepreg produced by impregnating a reinforcing fiber with a thermosetting resin composition is or are formed and laminated, followed by curing of the resin through the application of heat and pressure to obtain the FRP material.

The FRPs' properties depend on both the reinforcing fiber and the matrix resin. The important design properties include
tensile strength and modulus, compression strength and modulus, impact resistance, damage tolerance, and toughness. In general, the FRP materials are composed of about 60% by weight of the reinforcing fibers, which govern the majority of the properties, whereas the matrix resin has greatest effect on compression strength and transverse tensile properties.

Although existing FRP materials are well-suited for their intended use in providing high strength and toughness, there still is a continuous need for materials that have even higher levels of compression strength under different environmental conditions. The development of high performance resins where the flexural modulus is as high as possible without deleteriously affecting the other properties has been, and continues to be, a major goal in the aerospace composites industry.

State-of-the-art epoxy matrix resins systems in high performance composites are typically based on N,N',N'-tetraglycidyl 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl sulfone. These resins produce high tensile strength and tensile moduli. Epoxy resin systems providing higher matrix properties than state-of-the-art formulations are also known. For example, epoxy resin systems which use naphthalene-based epoxy resin systems in combination with amine curing agents provide higher compression strength and higher heat resistance than the state-of-the-art resin system, as disclosed in a number of patent publications, for example, U.S. Pat. Publications Nos. 20110049426 and 20130217283. Another epoxy resin system using a naphthalene-based epoxy resin system with a dicyclopentadiene-modified phenolic as a curing agent provides higher heat resistance, low water absorption, and good adhesion, as disclosed in U.S. Pat. No. 5312878. However, these systems are designed for high cure temperatures of above 150°C for at least 2 hours to achieve the desired maximum properties. In some applications, more than one curing agent can be used for low
temperature cure or out-of-a autoclave cure. For example, U.S. Patent Publication No. 20140100320 disclosed that an epoxy resin composite with aromatic amine and aliphatic amine in combination provides low temperature curability featuring high compression strength without deteriorating other mechanical properties. However, this epoxy resin composite has large amounts of water absorption, resulting in the hot/wet properties being impaired. Thus, there is still a need for matrix resins, particularly in the field of high performance materials, which afford higher compression strengths and moduli in combination with improved high heat resistance, low temperature curability, and a reduced tendency to absorb water.

The present invention therefore seeks to provide an epoxy resin composition that can be cured at a low temperature of below 150°C to form a cured product excellent in matrix resin modulus and heat resistance that prior attempts have failed to achieve. Another object is to provide an FRP material that is excellent under hot/wet conditions. It has been found that a composition containing a naphth alene-based epoxy resin having at least two naphthalene moieties and at least one glycidyl ether group per molecule and a combination of aromatic and aliphatic amine hardeners exhibits excellent flexural modulus, low water absorption, and low temperature curability. It is also believed that high matrix resin flexural modulus is directly correlated to high compression strength of the FRP materials. Additionally, the matrix resin with high heat resistance and low water absorption can provide significantly higher compression strength under hot/wet conditions.

Summary of the Invention

In one aspect of the invention, an epoxy resin composition for a fiber-reinforced composite material is provided, comprising components (A), (B), (C), (D), and (E), wherein the epoxy resin composition has a degree of cure of at least 90% and a water
absorption of at most 3.0 wt% after being cured at 132°C for 2 hours, where the components (A), (B), (C), (D), and (E) comprise:

(A) at least one naphthalene-based epoxy resin having at least two naphthalene moieties and at least one glycidyl ether group per molecule;

(B) at least one epoxy resin other than the naphthalene-based epoxy resin;

(C) at least one dicyandiamide;

(D) at least one diaminodiphenyl sulfone; and

(E) at least one urea-based catalyst.

This invention further includes a cured epoxy resin obtained by curing the above mentioned epoxy resin composition, a prepreg obtained by impregnating a reinforcing fiber matrix with the above mentioned epoxy resin composition, a fiber-reinforced composite material obtained by curing the prepreg, and a fiber-reinforced composite material comprising a cured product obtained by curing the above mentioned epoxy resin composition and a reinforcing fiber base prepreg.

As opposed to resin systems described in the prior art, the inventors have surprisingly discovered that when a naphthalene-based epoxy resin containing two or more naphthalene moieties per molecule is employed in an epoxy resin composition, it is possible to maintain a high modulus in a cured resin obtained by curing the epoxy resin composition at a low temperature of below 150°C while reducing the tendency of the cured resin to absorb water, thus obtaining a better overall hot/wet modulus when tested. This was unexpected, at least in part because the prior art publications employing such naphthalene-based epoxy resins only recognized that such epoxy resins result in greater toughening of cured resins. Normally, a bifunctional epoxy resin will reduce the overall modulus of the system so that even if the water absorption is reduced the hot/wet modulus will be impaired. For example,
when using a dicyclopentadiene-based epoxy resin, a well-known material for reducing water absorption, the water absorption of the cured resin is reduced but room temperature dry modulus is lower. Even though the lower water absorption helps retain a higher percentage of the dry modulus when tested under hot/wet conditions, the hot/wet modulus is not significantly increased since the dry modulus has been lowered due to the presence of the dicyclopentadiene-based epoxy resin.

**Detailed Description of Certain Embodiments of the Invention**

Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the invention.

The terms "approximately", "about" and "substantially" as used herein represent an amount close to the stated amount that still performs the desired function or achieves the desired result. For example, the terms "approximately", "about", and "substantially" may refer to an amount that is within less than 10% of, with in less than 5% of, with in less than 1% of, with in less than 0.1% of, or with in less than 0.01% of the stated amount.

The term "room temperature" as used herein has its ordinary meaning as known to those skilled in the art and may include temperatures within the range of about 15°C to 43°C.

The term "low temperature cure" as used herein includes curing at temperatures within the range of about 110°C to about 150°C.

Component (A) comprises one or more epoxy resins containing at least two naphthalene moieties and at least one glycidyl ether per molecule. Such epoxy resins are referred to herein as "naphthalene-based epoxy resins." The term
"napththalene" as used herein describes a structure of two benzene rings which are conjugated to each other directly. Any of the napththalene-based monomer precursors (such as hydroxyl-substituted bi-naphthalene) may be formed into a glycidyl epoxy resin, such as glycidyl ether epoxy resins. The diglycidyl ethers of the precursors may be formed by reacting the precursor with epichlorohydrin in the presence of a basic catalyst.

Without wishing to be bound by theory, it is believed that the napththalene-based epoxy resins, which form part of an epoxy resin composition as described herein, provide low water absorption, high flexural modulus and high heat resistance once the epoxy resin composition has been cured. Above mentioned component (A) is an essential component for an epoxy resin composition to successfully provide excellent performance, particularly under hot/wet conditions.

The napththalene-based epoxy resin may comprise one bi-naphthalene moiety to which at least one glycidyl ether substituent is bonded. More than one glycidyl ether substituent may be bonded to the bi-naphthalene moiety at any suitable position in any suitable combination. The bi-naphthalene moiety may also have a non-glycidyl ether substituent bonded at any of the non-glycidyl ether substituted sites of either napththalene ring. Suitable non-glycidyl ether substituent groups include, without limitation, hydrogen atom, halogen atoms, Cl to C₆ alkyl groups, C₁ to C₆ alkoxy groups, C₁ to C₆ fluoroalkyl groups, cycloalkyl groups, aryl groups, and aryloxy groups and combinations thereof. Such non-glycidyl ether substituent groups may be straight, branched, cyclic, or polycyclic substituents, wherein these groups are optionally employed individually or different groups are optionally employed in combination thereof.

The napththalene-based epoxy resin may contain two, three, four or more napththalene rings linked to each other either directly or through a linking (bridging) moiety, such as a methylene group
(−CH₂−), with at least one glycidyl ether group (preferably at least two glycidyl ether groups) being bonded to (substituted on) a naphthalene ring (or multiple naphthalene rings, where two or more glycidyl ether groups are present). The multiple naphthalene rings may optionally be substituted with one or more further substituents, including any of the aforementioned types of substituents. Thus, in various embodiments of the invention component (A) may be comprised of one or more naphthalene-based epoxy resins represented by the following Formula (1):

$\text{Formula (1)}$

wherein $n$ represents the number of repeating units and is an integer of 1 or more; $R_1$ to $R_8$ are each independently selected from the group consisting of a hydrogen atom, halogen atoms, C₁ to C₆ alkyl groups, C₁ to C₆ alkoxy groups, C₁ to C₆ fluoroalkyl groups, cycloalkyl groups, aryl groups, and arylalkyl groups wherein these groups are optionally employed individually or different groups are optionally employed in combination as each of $R_1$ to $R_8$; $Y_1$ and $Y_2$ are each independently selected from the group consisting of a hydrogen atom and a glycidyl ether group wherein these groups are optionally employed individually or different groups are optionally employed in combination as each of $Y_1$ and $Y_2$; and each X is independently selected from the group consisting of a direct bond, −CH₂−, −C(CH₃)₂−, −S−, −SO₂−, −O−, −C(=0)O−, −C(=0)NH−, C₁ to C₆ alkyl groups, C₁ to C₆ alkoxy groups, cycloalkyl groups, aryl groups
and aryloxy groups, wherein these groups are optionally employed individually or different groups are optionally employed in combination as X.

In another embodiment, component (A) may be comprised of epoxy resin represented by the following Formula (I):

(1D

wherein R₁ to R₁₂ are each independently selected from the group consisting of hydrogen atoms, halogen atoms, Cl to ClO alkyl groups, Cl to ClO alkoxyl groups, Cl to ClO fluoroalkyl groups, cycloalkyl groups, aryl groups, aryloxy groups, and glycidoxy groups, Y₁ to Y₇ are each independently selected from the group consisting of hydrogen atoms, halogen atoms, Cl to ClO alkyl groups, Cl to ClO alkoxyl groups, Cl to ClO fluoroalkyl groups, cycloalkyl groups, aryl groups, aryloxy groups, and glycidoxy groups, wherein each benzene nucleus may be substituted with one or more Y groups, n is 0 or an integer of 1 to 5, k is 0 or an integer of 1 to 3, wherein the Y groups may be attached to either or both rings of each naphthalene nucleus; and each X is independently selected from the group consisting of a direct bond, -CH₂-, -C(CH₃)₂-, -SO₂-, -O-, -C(=0)O-, -C(=0)NH-, Cl to C₆ alkylene groups, Cl to C₆ alkoxylene groups, cycloalkylene groups, arylene groups and aryloxylen groups, wherein these groups are optionally employed individually or different groups are optionally employed in combination as X.

The glycidyl ether groups on the naphthalene moieties may be bonded to any of the carbon atoms of each naphthalene ring in any combination. The glycidyl ether groups may therefore be
present at the 2, 3, 4, 5, 6, and/or 7 positions of any of the naphthylene rings present, and where there is more than one glycidyl ether group may be present in any suitable combination on any of the naphthylene rings of the epoxy resin.

Specific precursors which may be used for producing the naphthylene-based epoxy resin having two or more naphthylene moieties per molecule, by way of example, include 1-(2-hydroxy-naphthalen-1-yl methyl)-naphthalene-2-ol, 1-(2-hydroxy-naphthalen-1-yl methyl)-naphthalene-2,7-diol, 1-(2-hydroxy-naphthalen-1-yl methyl)-naphthalene-7-ol, 1-(7-hydroxy-naphthalen-1-yl methyl)-naphthalene-7-ol, 1-(2,7-dihydroxy-naphthalen-1-yl methyl)-naphthalene-2,7-diol, or any combination thereof. Such precursors may be reacted with epichlorohydrin, using base catalysis, to introduce the desired glycidyl ether groups as a result of the hydroxyl groups of the precursor reacting with the epichlorohydrin.

The chemical structures of specific exemplary (non-limiting) naphthylene-based epoxy resins suitable for use in the present invention are shown below.
where \( n \) is the number of repeating units and an integer of 1 or more.

The amount of component (A) (naphthalene-based epoxy resin) may be in the range of 20 to 70phr per 100phr of total epoxy resin. In certain embodiments, the amount of naphthalene-based epoxy resin may be in the range of 25 to 40phr or 25 to 35phr per 100phr of total epoxy resin. If the amount is less than 20phr, water absorption may be high and hot/wet flexural modulus may be low. If the amount is greater than 70phr, the resin viscosity may be very high and handling and processing of the FRP material may be difficult.

Examples of commercially available products suitable for use as component (A) include "Epiclon (registered trade mark)" HP4700, HP4710, HP4770, EXA4701, EXA4750, and EXA7240 (manufactured by Dainippon Ink and Chemicals, Inc.), NC-7000 L and NC-7300 L (manufactured by Nippon Kayaku Co., Ltd.) and ESN-175 and ESN-375 (manufactured by Tohto Kasei Epoxy Co., Ltd.), etc., as well as combinations thereof.

The epoxy resin composition comprising component (A) is capable of being cured at 132°C for 2 hours to achieve the degree of cure of at least 90%. If the degree of cure is less than 90%, the FRP material obtained will have low compressive strength and heat resistance. The cured epoxy resin composition also has a water absorption of at most 3.0 wt% after immersing in boiling water for
24 hours. If the water absorption is more than 3.0 wt%, the FRP material obtained will have low compressive strength and heat resistance, particularly under hot/wet conditions. The water absorption is measured by the difference in the weight of the epoxy resin composition before and after immersion.

The cured epoxy resin composition comprising component (A) may have a room temperature flexural modulus of at least 4.0 GPa and a hot/wet flexural modulus of at least 3.0 GPa. The room temperature flexural modulus refers to the sample being tested without immersion and the hot/wet flexural modulus refers to the sample being tested at 82°C after immersing in boiling water for 24 hours. If the hot/wet flexural modulus is less than 3.0 GPa, the FRP material obtained may have low compressive strength. The flexural modulus of the cured epoxy resin can be determined by 3-point bending test in accordance with ASTM D 7264 using an Instron Universal Testing Machine (manufactured by Instron).

In accordance with the invention, the epoxy resin composition also comprises the component (B) wherein the component (B) comprises or is an epoxy or more than one epoxy resin other than a naphthalene-based epoxy resin as defined herein and used as component (A), to improve the cross linking and processability. These epoxy resins (epoxies) may be prepared from precursors such as amines (e.g., epoxy resins prepared using diamines and compounds containing at least one amine group and at least one hydroxy group such as tetraglycidyl diaminodiphenyl methane, tetraglycidyl diaminodiphenyl ether, tetraglycidyl diaminodiphenylsulfone, tetraglycidyl diaminodiphenylamine, triglycidyl-p-aminophenol, triglycidyl-m-aminophenol, triglycidylaminocresol, and tetraglycidyl xylylenediamine and halogen-substituted products, alkynol-su bistituted products, hydroygenated products thereof and so on), phenols (e.g., bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, bisphenol R epoxy resins, phenol-novolac epoxy resins, cresol-
novolac epoxy resins, resorcinol epoxy resins and tri phenyl methane epoxy resins, dicyclopenta diene epoxy resins, naphthlene epoxy resins (epoxy resins containing only a single naphthlene moiety per molecule), epoxy resins having a biphenyl skeleton, isocyanate modified epoxy resins, epoxy resins having a fluorene skeleton, and compounds having a carbon-carbon double bond (e.g., alicyclic epoxy resins). It should be noted that the epoxy resins suitable for use in component (B) are not restricted to the examples above. Halogenated epoxy resins prepared by halogenating these epoxy resins can also be used. Furthermore, mixtures of two or more of these epoxy resins, and compounds having one epoxy group or monoepoxy compounds such as glycidyl aniline, glycidyl toluidine or other glycidyl amines (particularly glycidyl arylamines) can be employed in the formulation of the epoxy resin composition.

Examples of commercially available products include: amine base epoxy such as YH434 L (manufactured by Nippon Steel Chemical Co., Ltd.), "J ER (registered trade mark)" 604 (manufactured by Mitsui Chemical Corporation), "Sumiepoxy (registered trade mark)" ELM434 and, ELM100 (manufactured by Sumitomo Chemical Co., Ltd.), "Araldite (registered trade mark)" MY9 655T, MY0720, MY0721, MY0722, MY05 500, MY0 510, MY0600, and MY0610 (manufactured by Huntsman Advanced Materials), "J ER (registered trade mark)" 630 (manufactured by Mitsubishi Chemical Corporation), TETRAD-X and TETRAD-C (manufactured by Mitsubishi Gas Chemical Company, Inc.); bisphenol A epoxy resins such as "J ER (registered trade mark)" 825, 828, 834, 1001, 1002, 1003, 1003F, 1004, 1004AF, 1005F, 1006FS, 1007, 1009 and 1010 (manufactured by Mitsubishi Chemical Corporation), "Tactix (registered trade mark)" 123 (manufactured by Huntsman Advanced Materials); brominated bisphenol A epoxy resins such as "J ER (registered trade mark)" 505, 5050, 5051, 5054 and 5057
(manufactured by Mitsubishi Chemical Corporation); hydrogenated bisphenol A epoxy resins such as ST5080, ST4000D, ST4100D, and ST5100 (manufactured by Nippon Steel Chemical Co., Ltd.); bisphenol F epoxy resins such as "j ER (registered trademark)" 806, 807, 4002 P, 4004 P, 4007 P, 4009 P and 4010P (manufactured by Mitsubishi Chemical Corporation), and "Epotohto (registered trademark)" YDF2001 and YDF2004 (manufactured by Nippon Steel Chemical Co., Ltd.); tetra methyl -bisphenol F epoxy resin such as YSLV-80XY (manufactured by Nippon Steel Chemical Co., Ltd.); bisphenol S epoxy resins such as "Epiclon (registered trade mark)" EXA-154 (manufactured by Dainippon Ink and Chemicals, Inc.); phenol-novol ac epoxy resins such as "j ER (registered trademark)" 152 and 154 (manufactured by Mitsubishi Chemical Corporation), and "Epiclon (registered trademark)" N-740, N-770, and N-775 (manufactured by Dainippon Ink and Chemicals, Inc.); cresol-novol ac epoxy resins such as "Epiclon (registered trademark)" N-660, N-665, N-670, N-673, and N-695 (manufactured by Dainippon Ink and Chemicals, Inc.), and EOCN-1020, EOCN-102S and EOCN-104S (manufactured by Nippon Kayaku Co., Ltd.); resorcinol epoxy resins such as "Denacol (registered trade mark)" EX-201 (manufactured by Nagase Chemtex Corporation); naphthalene epoxy resins (containing a single naphthalene moiety per molecule) include HP4032 and HP4032D (manufactured by Dainippon Ink and Chemicals, Inc.), "Ara Idite (registered trademark)" MY 0816 (manufactured by Huntsman Advanced Materials); tri phenyl methane epoxy resins such as "j ER (registered trademark)" 1032S50 (manufactured by Mitsubishi Chemical Corporation), "Tactix (registered trademark)" 742 (manufactured by Huntsman Advanced Materials) and EPPN-501H (which are manufactured by Nippon Kayaku Co., Ltd.); dicyclopentadiene epoxy resins include "Epiclon (registered trademark)" HP7200, HP7200L, HP7200 H and HP7200 HH (manufactured by Dainippon Ink and Chemicals, Inc.), "Tactix (registered trademark)" 556
(manufactured by Huntsman Advanced Materials), and XD-1000-1L and XD-1000-2L (manufactured by Nippon Kayaku Co., Ltd.); epoxy resins having a biphenyl skeleton such as "j ER (registered trademark)" YX4000 H, YX4000 and YL6616 (manufactured by Mitsubishi Chemical Corporation), and NC-3000 (manufactured by Nippon Kayaku Co., Ltd.); isocyanate-modified epoxy resins such as AER4152 (manufactured by Asahi Kasei Epoxy Co., Ltd.) and ACR1348 (manufactured by ADEKA Corporation) each of which has an oxazolidone ring; epoxy resins having a fluorene skeleton such as PG-100, CG-200 and EG-200 (manufactured by Osaka Gas Chemicals Co., Ltd) and LME10169 (manufactured by Huntsman Advanced Materials); glycidylanilines such as GAN (manufactured by Nippon Kayaku Co., Ltd.), and glycidyl toluidines such as GOT (manufactured by Nippon Kayaku Co., Ltd.). Furthermore, more than one of these epoxies may be used in combination as component (B).

In some of the embodiments, the above-material component (B) may comprise component (B1) and component (B2) which are epoxy resins different from each other, wherein component (B1) is an epoxy resin having more than two epoxy-functional groups per molecule and component (B2) is an epoxy resin different from component (B1) and having less than three epoxy-functional groups per molecule. Without wishing to be bound by theory, it is believed that the component (B1) epoxy resin provides high cross linking and high strength once the composition has been cured. It is also believed that the component (B2) epoxy resin provides high elongation and low viscosity resin for handleability and tackiness. "Handleability" refers to the ability to easily handle and process the material.

The amount of component (B1) may be in the range of 30 to 80 phr per 100 phr of total epoxy resin. If the amount is less than 30 phr, the strength of the FRP material obtained may be impaired. If the amount is greater than 80 phr, the water absorption may be
high and the FRP material obtained may have low compression strength.

Examples of commercially available products suitable for use as component (B1) include: amine base epoxy resins such as YH434L (manufactured by Nippon Steel Chemical Co., Ltd.), "j ER (registered trademark) " 604 (manufactured by Mitsubishi Chemical Corporation), TG3DAS (manufactured by Konishi Chemical Ind. Co., Ltd.), "Su miepoxy (registered trade mark) " ELM434 and, ELM100 (manufactured by Sumitomo Chemical Co., Ltd.), "Araldite (registered trademark) " MY9655T, MY0720, MY0721, MY0722, MY0500, MY0510, MY0600, and MY0610 (manufactured by Huntsman Advanced Materials), "j ER (registered trademark) " 630 (manufactured by Mitsubishi Chemical Corporation), TETRAD-X and TETRAD-C (manufactured by Mitsubishi Gas Chemical Company, Inc.); phenol-novolac epoxy resins such as "j ER (registered trademark) " 152 and 154 (manufactured by Mitsubishi Chemical Corporation), and "Epicon (registered trademark) " W-740, N-770, and N-775 (manufactured by Dainippon Ink and Chemicals, Inc.).

In some embodiments, the component (B2) epoxy resin may have an epoxy equivalent weight of less than 205 g/eq to achieve high elongation. Examples of commercially available products suitable for use as component (B2) having an EEW of less than 205 g/eq include: bisphenol A epoxy resins such as "j ER (registered trademark) " 825, 828 and 834 (manufactured by Mitsubishi Chemical Corporation), "Tactix (registered trademark) " 123 (manufactured by Huntsman Advanced Materials); bisphenol F epoxy resins such as "Epicon (registered trademark) " 830 (manufactured by Dainippon Ink and Chemicals, Inc.), "j ER (registered trademark) " YL983 U, 806 and 807 (manufactured by Mitsubishi Chemical Corporation); and naphthalene epoxy resins (containing a single naphthalene moiety per molecule) such as "Epicon (registered trademark) " HP403 2 and HP403 2D (manufactured by Dainippon Ink and Chemicals, Inc.), and
"Araldite (registe red trade mark) " MY 0816 (manufactured by Huntsman Advanced Materials), etc.

In other embodiments, the component (B2) may have an epoxy equivalent weight of less than 170 g/eq to achieve even higher elongation. Additionally, these epoxies can provide lower resin viscosity for handleability, processability, and tackiness. Examples of commercially available products suitable for component (B2) having an epoxy equivalent weight of less than 170 g/eq include: GAN (manufactured by Nippon Kayaku Co., Ltd.) and cycloaliphatic epoxy resins such as "Celoxide (registe red trade mark) " 2021P, 8000, 8010, and 8200 (manufactured by Daicel Chemical Industries).

The amount of component (B2) may be at most 30phr per loophr of total epoxy resin. If the amount is greater than 30phr, the water absorption may be high and the FRP material obtained may have low compression strength.

The viscosity of the epoxy resin composition comprising the component (B2) at 40°C may be between $1 \times 10^3$ and $3 \times 10^4$ Pa-s, in order to achieve both handleability and processability of the FRP while maintaining the mechanical properties. If the viscosity at 40°C is too low, the handleability may be compromised because the tack may be too high. If the viscosity at 40°C is too high, the moldability of the FRP may be unsatisfactory because the tack may be too low. The viscosity of the epoxy resin composition was measured using a dynamic viscoelasticity measuring device (ARES, manufactured by TA Instruments) using parallel plates with a diameter of 40 mm while increasing the temperature at a rate of 2°C/min, with a strain of 10%, frequency of 0.5 Hz, and plate interval of 1 mm, from 40°C to 150°C.

As a curing agent, a combination of amine-based curing agents is suitable for curing the epoxy resin composition. An amine-based curing agent is a compound that contains a nitrogen atom in the molecule and can react with epoxy groups for curing.
Without wishing to be bound by theory, it is believed that the combination of amine-based curing agents utilized in the present invention provides high heat resistance and storage stability.

In accordance with the invention, components (C) and (D) are used together as curing agents. Said combination provides the FRP material with low temperature curability while simultaneously providing superior compression strength, heat resistance, and storage stability. The suitable amine curing agents for component (C) and (D) are dicyandiamide and dianinodiphenyl sulfone, respectively. Specific illustrative examples of suitable dianinodiphenyl sulfones include, but are not limited to, 4,4'-dianinodiphenyl sulphone (4,4'-DDS) and 3,3'-dianinodiphenyl sulphone (3,3'-DDS) and combinations thereof.

The amount of component (C) may be in the range of 2 to 7 phr per 100 phr of total epoxy resin. If the amount is less than 2 phr, the heat resistance and mechanical properties of FRP material obtained may be impaired. If the amount is greater than 7 phr, the water absorption may be high from unreactive amine and the FRP material obtained may have low compression strength under hot/wet conditions.

The amount of component (D) may be in the range of 5 to 30 phr per 100 phr of total epoxy resin. If the amount is less than 5 phr, the heat resistance and mechanical properties of FRP material obtained may be impaired. If the amount is greater than 30 phr, the viscosity of the epoxy resin composition may become too high; the processing and moldability of the FRP material may also be adversely affected.

Examples of commercially available products suitable for component (C) include DICY-7 and DICY-15 (manufactured by Mitsubishi Chemical Corporation) and "Dyhard (registered trademark)" 100S (manufactured by AlzChem Trostberg GmbH). A micronized grade of dicyandiamide is utilized in one embodiment of the present invention. These curing agents may be supplied as a
powder or can be employed in the form of a mixture with a liquid epoxy resin composition. Examples of commercially available products suitable for component (D) include "Arad ur (registered trade mark)" 9664-1 and 979 1-1 (manufactured by Huntsman Advanced Materials).

In other embodiments, any curing agents other than the abovementioned components (C) and (D) may be added to the epoxy resin composition, as long as the effect of the invention is not deteriorated. Examples of other curing agents include polyamides, aromatic amidoamines (e.g., aminobenzamide, aminobenzanilides, and aminobenzene sulfonamides), aromatic diamines (e.g., diamino diphenyl methane, and m-phenyl enediamine), tertiary amines (e.g., N,N-dimethylaniline, N,N-dimethyl benzylamine, and 2,4,6-tris(dimethylaminomethyl)phenol), aminobenzoates (e.g., tri methyleneglycol di-p-aminobenzoate and neopentylyglycol di-p-aminobenzoate), aliphatic amines (e.g., diethylenetriamine, tri ethylentetraamine, isophorondiamine, bis(aminomethyl)norbormane, bis(4-aminocyclohexyl)methane, dimer acid esters of polyethyl eneimine), imidazole derivatives (e.g., 2-methylimidazole, 1-benzyl-2-methylimidazole, 2-ethyl-4-methylimidazole), carboxylic acid anhydrides (e.g., methyl hexahydrophthalic anhydride), carboxylic acid hydrazides (e.g., adipic acid hydrazide, naphthalene-1-carboxylic acid hydrazide), tetra methyl guanidine, carboxylic acid amides, polyphenol compounds, polysulfides and mercaptans, and Lewis acids and bases (e.g., boron trifluoride ethylene mine and tris-(diethy1aminomethyl) phenol), etc.

Furthermore, a latent curing agent can be also be used since it makes the storage stability of the epoxy resin composition excellent. A latent curing agent is a curing agent capable of exhibiting activity owing to the phase change or chemical change, etc. caused by certain stimulation such as heat or light. As the latent curing agent, an amine adduct type latent curing agent,
microcapsule type latent curing agent, dicyandiamide derivatives, the role of curing agent is used.

An amine adduct type latent curing agent is a product having a high molecular weight and made insoluble at the storage temperature, obtained by reacting an active ingredient such as a compound having a primary, secondary or tertiary amine or any of various imidazole derivatives react with a compound capable of reacting with those compounds. A microcapsule type latent curing agent is a product obtained by using a curing agent as a nucleus and covering the nucleus with a shell such as a high molecular substance, for example, an epoxy resin, polyurethane resin, polystyrene-based compound or polyamide, etc., or cyclodextrin, etc., to decrease the contact between the epoxy resin and the curing agent. A dicyandiamide derivative is obtained by combining dicyandiamide with any of various compounds, and a product obtained by reaction with an epoxy resin and a product obtained by reaction with a vinyl compound or acrylic compound, etc., can be enumerated.

Examples of commercially available products of the amine adduct type latent curing agent includes: "Amicure (registered Trademark)" PN-23, PN-H, PN-40, PN-50, PN-F, MY-24 and MY-H (manufactured by Ajinomoto Fine-Technology Co., Inc.), "Adeka Hardener (registered trademark)" EH-3293S, EH-3615S and EH-4070S (manufactured by Adeka Corporation). Examples of commercially available products of the microcapsule type latent curing agent include "Novacure (registered trademark)" HX-3721 and HX-3722 (manufactured by Asahi Kasei Chemicals Corporation). Examples of commercially available products of dicyandiamide derivative include DICY-7 and DICY-15 (manufactured by Japan Epoxy Resins Co., Ltd.). Any of the above-mentioned curing agents can be used more than two in combination, as long as the effect of the invention is not deteriorated.

In certain embodiments of the invention, the relative amounts of curing agent and epoxy resin in the epoxy resin
composition are selected such that there is a molar excess of epoxy groups relative to active hydrogens. For example, components (A), (B), (C) and (D) may each be present in an amount effective to provide a molar ratio of active hydrogens:epoxy groups of from 0.4:1 to 0.8:1. Formulations having a ratio lower than 0.4:1 may have low heat resistance and reduced properties, whereas formulations having a ratio higher than 0.8:1 may have lower reactivity and may not reach a high degree of cure at lower temperatures.

It has been discovered that the epoxy resin composition must be used with at least one curing catalyst to accelerate curing of the epoxy resin composition, so that the capability of achieving a high degree of cure (e.g., at least 90%) at a relatively low temperature (e.g., 132°C) with in a short period of time (two hours) is plausible.

In accordance with the present invention, the component (E) is the curing catalyst, wherein the curing catalyst is one or more urea-based compounds that can accelerate the reaction of epoxy resin with any curing agents and/or the self-polymerization of epoxy resin. Without wishing to be bound by theory, it is believed that the epoxy resin composition using urea-based catalysts as the curing catalyst has high storage stability and high heat resistance.

The amount of the component (E) may be in the range of 1 to 8phr per 100phr of total epoxy resin. If the amount is less than 1phr, the acceleration effect may be insufficient; the heat resistance of the FRP material obtained may be impaired. If the amount of is greater than 8phr, the accelerating effect may be excessive, the storage stability of the epoxy resin composition and the mechanical properties of the FRP material obtained may be impaired.

As used herein, the term "urea-based catalyst" means a compound containing at least one urea group (N(=O)N, wherein the nitrogen atoms are substituted with H and/or organo groups)
and capable of catalyzing the curing of the epoxy resin composition when heated. Suitable urea-based catalysts for component (E) include, for instance, aromatic urea catalysts containing at least one urea group (ωC(=O)N) and at least one aromatic group (e.g., phenyl, substituted phenyl, naphthyl, etc.). Illustrative examples of suitable urea-based catalysts include: N,N-dimethyl-N'-[(3,4-dichlorophenyl) urea, toluene bis(dimethyl urea), 4,4'-methyle ne bis (phenyl dimethyl urea), N-(4-chlorophenyl) N,N-dimethyl urea and 3-phenyl-1,1-dimethyl urea, and combinations thereof.

Examples of commercially available urea-based catalysts suitable for use as component (E) include: DCM U99 (manufactured by Hodogaya Chemical Co., Ltd.), "Dyhard (registred trad emark)" UR200, UR300, UR400, UR500, URAccl 3 and URAcc5 7 (manufactured by AlzChem Trostberg GmbH.), and "Omicure (registred trad emark)" 24, 24M, 52 and 94 (manufactured by CVC Specialty Chemicals, Inc.). Among these, urea-based catalysts having more than one urea group per molecule may be used in order to attain particularly rapid curing properties.

In other embodiments, any curing catalyst(s) other than the urea-based catalysts may also be added, as long as the effect of the invention is not deteriorated. Examples of such curing catalysts include boron trifluoride piperidine, p-t- butyl catechol, sulfonate compounds (e.g., ethyl p-toluene sulfonate, isopropyl p-toluenesulfonate or methyl p-toluenesulfonate), tertiary amines and salts thereof, imidazoles and salts thereof, phosphorus curing accelerators, metal carboxylates and Lewis and Brønsted acids and salts thereof. Examples of commercially available imidazole compounds or derivatives thereof include 2MZ, 2PZ and 2E4MZ (manufactured by Shikoku Chemicals Corporation). Examples of suitable Lewis acid catalysts include complexes of a boron trihalide and a base, such as a boron trifluoride piperidine complex, boron trifluoride monoethyl amine complex, boron trifluoride triethanol amine complex, or boron trichloride octyl amine complex. Any two
or more of the abovementioned curing catalysts can be used in combination as long as the effect of the invention is not detriorated.

The epoxy resin composition comprising the abovementioned components (A) - (E) have a degree of cure (DoC) of at least 90% after heating at 132°C for 2 hours. The DoC of an epoxy resin composition can be determined by Differential Scanning Calorimetry (DSC, manufactured by TA Instruments). The DoC value is obtained by empirically comparing the exothermic reaction peak area of an uncured resin (∆H_{uncured}) against the residual exothermic reaction peak area of a cured resin (∆H_{cured}). An epoxy resin composition may exhibit more than one exothermic reaction peak; in such cases, the total areas of such peaks are compared. Herein, the DoC can be calculated by the following formula:

\[
\text{Degree of Cure, DoC (\%)} = \frac{\Delta H_{cured} - \Delta H_{uncured}}{\Delta H_{uncured}} \times 100
\]

where: ∆H_{uncured} = exothermic reaction peak area of an uncured resin

∆H_{cured} = exothermic reaction peak area of a cured resin

The epoxy resin composition comprising the abovementioned components (A) - (E) may have a dry Tg (glass transition temperature) of at least 140°C and a wet Tg of at least 115°C when fully cured. Said "fully cured" epoxy resin is a cured epoxy resin where the degree of cure degree is 90% or more after heating at 132°C for 2 hours. The dry Tg refers to the glass transition temperature of a sample being tested without immersion and the wet Tg refers to the glass transition temperature of a sample being tested after immersing in boiling water for 24 hours. If the wet Tg is less than 115°C, the FRP material will have low heat resistance and low compression strength.
In certain embodiments, the cure profile is not particularly limited, as long as the effect of the invention is not deteriorated. If a higher Tg is desired, the epoxy resin composition can be cured at higher temperature. For example, the epoxy resin composition may have a dry Tg of 170°C and a wet Tg of 150°C when the composition is cured at 180°C for 2 hours. The Tg of a cured epoxy resin can be determined by torsional Dynamic Mechanical Analyzer (ARES, manufactured by TA Instruments).

In some embodiments, thermoplastic resins may be added to the epoxy resin composition, as long as the effect of the invention is not deteriorated. Without wishing to be bound by theory, it is believed that thermoplastic resins provide maximum fracture toughness and impact resistance. Such thermoplastic resins include, but are not limited to, elastomers, branched polymers, hyperbranched polymers, dendrimers, rubbery polymers, rubbery copolymers, block copolymers, and core-shell particles, with or without surface modification or functionalization. Examples of suitable thermoplastic resins include thermoplastic resins that are soluble in an epoxy resin and organic particles such as rubber particles and thermoplastic resin particles. As the thermoplastic resin that is soluble in an epoxy resin, a thermoplastic resin having a hydrogen-binding functional group, which may have an effect of improving the adhesion between a cured epoxy resin and a reinforcing fiber, may be used. Examples of thermoplastic resins which are soluble in an epoxy resin and have hydrogen-binding functional groups include the thermoplastic resins having one or more alcoholic hydroxy groups, thermoplastic resins having one or more amide bonds, and thermoplastic resins having one or more sulfonyle groups. Furthermore, the thermoplastic resin can be crystalline or amorphous.

Examples of thermoplastic resins having hydroxyl groups include polyvinyl alcohol resins such as polyvinyl formal and polyvinyl butyral, polyvinyl alcohols and phenoxy resins. Examples
of thermoplastic resins having amide bonds include polyamide, polyimide and polyvinyl pyrrolidone. An example of a thermoplastic resin having one or more sulfonyl groups is polysulfone. The polyamide, the polyimide and the polysulfone may have a functional group such as an ether bond and a carbonyl group in the main chain of the resin. The polyamide may have a substituent on a nitrogen atom in the amide group.

Examples of commercially available thermoplastic resins soluble in an epoxy resin and having a hydrogen-binding functional group include: polyvinyl acetal resins such as "Denkabutyral (registered trademark)" and "Denkaformal (registered trademark)" (manufactured by Denki Kagaku Kogyo Kabushiki Kaisha) and "Vinylec (registered trademark)" (manufactured by JNC Corporation); phenox resin such as "UCAR (registered trademark)" PKH P (manufactured by Union Carbide Corporation); polyamide resins such as "Macromelt (registered trademark)" (manufactured by Henkel-Hakusui Corporation) and "Amilan (registered trademark)" CM4000 (manufactured by Toray Industries Inc.); polyimides such as "Ultem (registered trademark)" 1000P (manufactured by General Electric Co., Ltd.) and "Matri mid (registered trademark)" 5218 (manufactured by Ciba Inc.); polysulfones such as "SumikaExcel (registered trademark)" PES 5003P and PES 2603 MP (manufactured by Sumitomo Chemical Co., Ltd.), "UDEL (registered trademark)" (manufactured by Solvay Advanced Polymers Kabushiki Kaisha), and "Virantage (registered trademark)" VW-10700 RFP (manufactured by Solvay Plastics); and polyvinyl pyrrolidone such as "Luviskol (registered trademark)" (manufactured by BASF Japan Ltd.). Suitable polyether sulfones, for example, may have a number average molecular weight of from about 10,000 to about 75,000 g/mol.

For certain embodiments, any type(s) of additive(s) may be added, as long as the effect of the present invention is not deteriorated. Rubber particles may be added. As for the rubber
particles, crosslinked rubber particles and core-shell rubber particles produced by the graft polymerization of different polymers on the surfaces of crosslinked rubber particles may be used, from the viewpoint of handling properties.

Examples of commercially available crosslinked rubber particles include FX501P (manufactured by Japan Synthetic Rubber Corpo ratio n), which comprises a crosslinked product of a carboxyl-modified butadiene-acrylonitrile copolymer, and CX-MN series (manufactured by Nippon Shokubai Co., Ltd.) and YR-500 series (manufactured by Nippon Steel Chemical Co., Ltd.), each of which comprises acrylic rubber micro particles.

Examples of commercially available core-shell rubber particle products include "Paraloid (registered trademark)" EXL-2655 (manufactured by Kureha Corpo ratio n), which comprises a butadiene-alkyl methacrylate-styrene copolymer, "Styroloid (registered trademark)" AC-3355 and TR-2122 (manufactured by Takeda Pharmaceutical Co., Ltd.), each of which comprises an acrylic acid ester-methacrylic acid ester copolymer, "PARALOID (registered trademark)" EXL-2611 and EXL-3387 (manufactured by Rohm & Haas) each of which comprises a butyl acrylate-methyl methacrylate copolymer, and "Kane Ace (registered trademark)" MX series (manufactured by Kaneka Corpo ratio n).

The acrylic resin has high incompatibility with an epoxy resin, and therefore may be used suitably for controlling viscoelasticity.

Examples of commercially available acrylic resin products include "Dianal (registered trademark)" BR series (manufactured by Mitsuboshi Rayon Co., Ltd.), "Matsuno Micro-sp here (registered trademark)" M, M100 and M500 (manufactured by Matsuno Moto Yushi-Seiya kku Co., Ltd.), and "Nanostre nth (registered trademark)" E40 F, M22N and M52N (manufactured by Arkena).

As for the thermoplastic resin particles, polyamide particles and polyimide particles may be used. Polyamide particles are most preferable for greatly increasing the impact resistance due to their
excel lent tough ness. Among the polyam ides, nylon 12, nylon 11, nylon 6, nylon 6/12 copolymer, and a nylon (semi-IPN nylon) modified to have a semi-IPN (interpenetrating polymer network) with an epoxy compound as disclosed in Example 1 of Japanese Patent Application Laid-open No. 1-104624 impart particularly good adhesive strength in combination with the epoxy resin.

Examples of suitable commercially available polyamide particles include SP-500 (manufactured by Toray Industries Inc.) and "Orgasol (registered trademark)" (manufactured by Arkema), "Grilamid (registered trademark)" TR-55 (manufactured by EMS-Grivory), and "Trogamid (registered trademark)" CX (manufactured by Evonik).

Furthermore, any type of inorganic particle such as clay may be added, as long as the effect of the present invention is not deteriorated. Examples of suitable inorganic particles include metallic oxide particles, metallic particles and mineral particles. The inorganic particles may be used to improve some functions of the cured epoxy resin composition and to impart one or more functions to the cured epoxy resin composition. Examples of such functions include surface hardness, anti-blocking property, heat resistance, barrier property, conductivity, antistatic property, electro magnetic wave absorption, UV shield, toughness, impact resistance, and low coefficient of linear thermal expansion. Examples of other suitable inorganic materials include aluminum hydroxide, magnesium hydroxide, glass beads, glass flakes and glass balloons.

Examples of suitable metallic oxides include silicon oxide, titanium oxide, zirconium oxide, zinc oxide, tin oxide, indium oxide, aluminum oxide, antimony oxide, cerium oxide, magnesium oxide, iron oxide, tin-doped indium oxide (ITO), antimony-doped tin oxide and fluorine-doped tin oxide. Examples of suitable metals include gold, silver, copper, aluminum, nickel, iron, zinc and stainless.
Examples of suitable minerals include montmorillonite, talc, mica, boehmite, kaolinite, smectite, xenotlite, vermiculite and sericite. Examples of other suitable carbonaceous materials include carbon black, acetylene black, Ketjen black, carbon nanotubes, graphenes, carbon nanofibers, carbon nanobeads, fullerenes, etc.

Any size of inorganic particles may be used; for example, the inorganic particles may have a size which is in the range of 1 nm to 10 μm. Any shape inorganic particles may be used; for example, the inorganic particles may be spherical, needle, plate, balloon or hollow in shape. The inorganic particles may be just used as powder or used as a dispersion in a solvent like sol or colloid. Furthermore, the surface of the inorganic particle may be treated by a coupling agent to improve the dispersibility and the interfacial affinity with the epoxy resin.

In certain embodiments, the epoxy resin composition may contain one or more other materials in addition to the above mentioned materials, as long as the effect of the present invention is not deteriorated. Examples of other materials include mold release agents, surface treatment agents, flame retardants, antibacterial agents, leveling agents, antifoam agents, thixotropic agents, heat stabilizers, light stabilizers, UV absorbers, pigments, coupling agents and metal alkoxides.

The components of the epoxy resin composition may be mixed in a kneader, planetary mixer, triple roll mill, twin screw extruder, and the like. The epoxy resins and any the molding resins, excluding curing agents and catalysts, are added in the selected equipment. The mixture is then heated to a temperature in the range of 130 to 180°C while being stirred so as to uniformly dissolve the epoxy resins. After this, the mixture is cooled down to a temperature of no more than 100°C, while being stirred, followed by the addition of the curing agent and catalysts and kneading to disperse those components. This method may be used
to provide an epoxy resin composite with excellent storage stability.

There are no specific limitations or restrictions on the type of reinforcing fiber can be used, as long as the effects of the invention are not deteriorated. Examples include glass fibers, carbon fibers, and graphite fibers such as S glass, S-1 glass, S-2 glass, S-3 glass, E-glass, L-glass organic fibers such as aramid fibers, boron fibers, metal fibers such as alumina fibers, silicon carbide fibers, tungsten carbide fibers, and natural/bio fibers.

Particularly, carbon fiber may provide the FRP materials exceptionally high strength and stiffness as well as lightweight. Examples of carbon fibers are those from Toray Industries having a standard modulus of about 200-250 GPa (Torayca® T300, T300J, T400 H, T600 S, T700 S, T700G), an intermediate modulus of about 250-300 GPa (Torayca® T800 H, T800 S, T1000 G, T1100 G, M30 S, M30 G), or a high modulus of greater than 300 GPa (Torayca® M40, M35 J, M40 J, M46 J, M50 J, M55 J, M60 J). Among these carbon fibers, one with standard modulus, strength of 4.9 GPa or higher and elongation of 2.1% or higher is used in the examples.

The form and the arrangement of a layer of reinforcing fibers used are not specifically limited. Any of the forms and spatial arrangements of the reinforcing fibers known in the art such as long fibers in a direction, chopped fibers in random orientation, single tow, narrow tow, woven fabrics, mats, knitted fabrics, and braids may be employed. The term "long fiber" as used herein refers to a single fiber that is substantially continuous over 10 mm or longer or a fiber bundle comprising the single fibers. The term "short fibers" as used herein refers to a fiber bundle comprising fibers that are cut into lengths of shorter than 10 mm.

Particularly in the end use applications for which high specific strength and high specific elastic modulus are desired, a form where in a reinforcing fiber bundle is arranged in one direction may
be most suitable. From the viewpoint of ease of handling, a cloth-like (woven fabric) form is also suitable for the present invention.

The FRP materials of the present invention may be manufactured using methods such as the prepreg lamination and molding method, resin transfer molding method, resin film infusion method, hand lay-up method, sheet molding compound method, filament winding method and pultrusion method, though no specific limitations or restrictions apply in this respect.

The resin transfer molding method is a method in which a reinforcing fiber base material is directly impregnated with a liquid thermosetting resin composition and cured. Since this method does not involve an intermediate product, such as a prepreg, it has great potential for molding cost reduction and is advantageously used for the manufacture of structural materials for spacecraft, aircraft, rail vehicles, automobiles, marine vessels, and so on.

The prepreg lamination and molding method is a method in which a prepreg or prepregs, produced by impregnating a reinforcing fiber base material with a thermosetting resin composition, is/are formed and/or laminated, followed by the curing of the resin through the application of heat and pressure to the formed and/or laminated prepreg/prepregs to obtain a FRP material.

The filament winding method is a method in which one to several tens of reinforcing fiber rovings are drawn together in one direction and impregnated with a thermosetting resin composition as they are wrapped around a rotating metal core (mandrel) under tension at a predetermined angle. After the wraps of rovings reach a predetermined thickness, it is cured and then the metal core is removed.

The pultrusion method is a method in which reinforcing fibers are continuously passed through an impregnating tank filled with a liquid thermosetting resin composition to impregnate them with the thermosetting resin composition, followed by a squeeze die and
heating die for molding and curing, by continuously drawing them using a tensile machine. Since this method offers the advantage of continuously molding FRP materials, it is used for the manufacture of FRP materials for fishing rods, rods, pipes, sheets, antennas, architectural structures, and so on. Of these methods, the prepreg lamination and molding method may be used to give excellent stiffness and strength to the FRP materials obtained.

Prepregs may contain the epoxy resin composition and reinforcing fibers. Such prepregs may be obtained by impregnating a reinforcing fiber base material with an epoxy resin composition of the present invention. Impregnation methods include the wet method and hot melt method (dry method).

The wet method is a method in which reinforcing fibers are first immersed in a solution of an epoxy resin composition, created by dissolving the epoxy resin composition in a solvent, such as methyl ethyl ketone or methanol, and recovered, followed by the removal of the solvent through evaporation via an oven, etc. to impregnate reinforcing fibers with the epoxy resin composition. The hot-melt method may be implemented by impregnating reinforcing fibers directly with an epoxy resin composition, made fluid by heating in advance, or by first coating a piece or pieces of release paper or the like with an epoxy resin composition for use as resin film and then placing a film over one or either side of reinforcing fibers as configured into a flat shape, followed by the application of heat and pressure to impregnate the reinforcing fibers with the resin. The hot-melt method may give the prepreg having virtually no residual solvent in it.

The prepreg may have a carbon fiber areal weight of between 40 to 350 g/m². If the carbon fiber areal weight is less than 40 g/m², there may be insufficient fiber content, and the FRP material may have low strength. If the carbon fiber areal weight is more than 350 g/m², the drapability of the prepreg may be impaired. The prepreg may also have a resin content of between 20 to
70wt%. If the resin content is less than 20 wt%, the impregnation may be unsatisfactory, creating a large number of voids. If the resin content is more than 90 wt%, the FRP mechanical properties will be impaired.

Appropriate heat and pressure may be used under the prepreg lamination and molding method, the press molding method, autoclave molding method, bagging molding method, wrapping tape method, internal pressure molding method, or the like.

The autoclave molding method is a method in which prepregs are laminated on a tool plate of a predetermined shape and then covered with bagging film, followed by curing, performed through the application of heat and pressure while air is drawn out of the laminate. It may allow precision control of the fiber orientation, as well as providing high-quality molded materials with excellent mechanical characteristics, due to a minimum void content. The pressure applied during the molding process may be 0.3 to 1.0 MPa, while the molding temperature may be in the 90 to 300°C range (in one embodiment of the invention, in the range of 110°C to 150°C, e.g., 120°C to 140°C).

The wrapping tape method is a method in which prepregs are wrapped around a mandrel or some other cored bar to form a tubular FRP material. This method may be used to produce golf shafts, fishing poles, and other rod-shaped products. In more concrete terms, the method involves the wrapping of prepregs around a mandrel, wrapping of wrapping tape made of the non-plastic film over the prepregs under tension for the purpose of securing the prepregs and applying pressure to them. After curing of the resin through heating inside an oven, the cored bar is removed to obtain the tubular body. The tension used to wrap the wrapping tape may be 20 to 100 N. The curing temperature may be in the 80 to 300°C range (in one embodiment of the invention, in the range of 110°C to 150°C, e.g., 120°C to 140°C).
The internal pressure forming method is a method in which a preform obtained by wrapping prepregs around a thermoplastic resin tube or some other internal pressure applicator is set inside a metal mold, followed by the introduction of high pressure gas into the internal pressure applicator to apply pressure, accompanied by the simultaneous heating of the metal mold to mold the prepregs. This method may be used when forming objects with complex shapes, such as golf shafts, bats, and tennis or badminton rackets. The pressure applied during the molding process may be 0.1 to 2.0 MPa. The molding temperature may be between room temperature and 300°C or in the 180 to 275°C range (in one embodiment of the invention, in the range of 110°C to 150°C, e.g., 120°C to 140°C).

The FRP materials that contain cured epoxy resin compositions obtained from epoxy resin compositions of the present invention and reinforcing fibers are advantageously used in general industrial applications, and aeronautics and space applications. The FRP materials may also be used in other applications such as sports applications (e.g., golf shafts, fishing rods, tennis or badminton rackets, hockey sticks and ski poles) and structural materials for vehicles (e.g., automobiles, bicycles, marine vessels and rail vehicles, drive shafts, leaf springs, windmill blades, pressure vessels, flywheel s, papermaking rollers, roofing materials, cables, and repair/reinforcement materials).

Examples

The present embodiments are now described in more detail by way of examples. The measurement of various properties was carried out using the methods described below. Those properties were, unless otherwise noted, measured under environmental conditions comprising a temperature of 23°C and a relative humidity of 50%. The components used in the examples are as follows:
**Component (A)**

Naphthale-based epoxy resin, "EpiClon (registered trademark)" HP-4770 (manufactured by Dainippon Ink and Chemicals, Inc.) having an epoxide equivalent weight (EEW) of 205 g/eq.

Naphthale-based epoxy resin, "NC-7000 L" (manufactured by Nippon Kayaku) having an epoxide equivalent weight (EEW) of 230 g/eq.

**Component (B)**

Naphthale epoxy resin, "Ara Idite (registered trademark)" MY0816 (manufactured by Huntsman Advanced Materials) having a single naphthale moiety per molecule and an epoxide equivalent weight (EEW) of 150 g/eq.

**Component (B1)**

Tetraglycidyl diaminodiphenylmethane, "Ara Idite (registered trademark)" MY9655T (manufactured by Huntsman Advanced Materials) having an epoxide equivalent weight (EEW) of 120 g/eq.

Tetraglycidyl diaminodiphenylmethane, "Ara Idite (registered trademark)" MY0721 (manufactured by Huntsman Advanced Materials) having an epoxide equivalent weight (EEW) of 115 g/eq.

**Component (B2)**

Bisphenol A epoxy resin, "Epon (registered trademark)" 828 (manufactured by Momentive Specialty Chemicals) having an epoxide equivalent weight (EEW) of 185 g/eq.

Diglycidyl p-aminiline (GAN) (manufactured by Nippon Kayaku Co., Ltd.) having an epoxide equivalent weight (EEW) of 125 g/eq.

Cycloaliphatic epoxy, "Celloxi (registered trademark)" Cel-8000 (manufactured by Daicel Chemical Industries) having an epoxide equivalent weight (EEW) of 100 g/eq.
Component (C)

Dicyandiamide, "Dyhard (registered trademark)" 100S (manufactured by AlzChem Trostbe rg GmbH).

Component (D)

4,4'-Diaminodiphenylsulfone (4,4'-DDS), "Aradur (registered trademark)" 9664-1 (manufactured by Huntsman Advanced Materials).

3,3'-Diaminodiphenylsulfone (3,3'-DDS), "Aradur (registered trademark)" 9791-1 (manufactured by Huntsman Advanced Materials).

Component (E)

2,4'-Toluene bis dimethyl urea, "Omicure (registered trademark)" U-24M (manufactured by CVC Thermoset Specialties).

3-(3,4-Dichlorophenyl)-1,1-dimethyl urea, "Dyhard (registered trademark)" UR200 (manufactured by AlzChem Trostbe rg GmbH).

"Dyhard (registered trademark)" URAcc13 (manufactured by AlzChem Trostberg GmbH).

4-Methylenediphenylene bisdimethyl urea, "Dyhard (registered trademark)" UR400 (manufactured by AlzChem Trostberg GmbH).

[4-(Acetyloxy)phenyl]dimethylfluorone, (OC-6-11)-hexafluorooctadecylmonate (1-), "San-Aid (registered trademark)" SI-150 (manufactured by Sanshin Chemical Industry Co., Ltd.).

Thermoplastic Resin

Polyethersulfone with a terminal hydroxyl group, "Sumikaexcel (registered trademark)" PES 5003 P (manufactured by Sumitomo Chemical Co., Ltd.) having a number average molecular weight of 47,000 g/mol.

Polyethersulfone, "Virtanage (registered trademark)" VW10700RFP polyethersulfone (manufactured by Solvay Advanced Polymers) having a number average molecular weight of 21,000 g/mol.
**Carbon Fibers**

Plain Weave Carbon fiber, "Torayca (registered trademark)" T700S-12K-50C having a fiber filament count of 12,000, tensile strength of 4.9 GPa, tensile elasticity of 230 GPa, and tensile elongation of 2.0% (manufactured by Toray Industries Inc.).

**Methods**

The following methods were used to prepare and measure the epoxy resin composition, the prepreg and the FRP material for each example.

1. **Resin Mixing**

   A mixture was created by dissolving presribed amounts of all the components other than the curing agent and curing accelerator in a mixer, and then prescribed amounts of the curing agent were mixed into the mixture along with prescribed amounts of the accelerator to obtain the epoxy resin composition.

2. **Cured Profile**

   The cured epoxy resin composition was molded by the following method described in this section. After mixing, the epoxy resin composition prepared in (1) was injected into a mold set for a thickness of 2 mm using a 2 mm-thick "Teflon (registered trademark)" spacer. Then, the epoxy resin composition was heated at a rate of 1.7°C/min from room temperature to 132°C and then kept for 2 hours at 132°C to obtain 2 mm-thick cured epoxy resin composition plates.

3. **Degree of Cure**

   In other embodiments of the present invention, the epoxy resin composition may be cured to have a certain degree of cure. The percent cure or degree of cure (DoC) of an epoxy resin composition can be determined using a Differential Scanning Calorimeter (DSC) (Q200 with an RCS (mechanical refrigeration cooling system), manufactured by TA Instruments). The degree of cure is empirically determined by comparing the exothermic reaction peak area of an uncured resin \(\text{AH}_{\text{uncured}}\) against the
residual exothermic reaction peak area of a cured resin ($\Delta H_{\text{cured}}$), using a ramp rate of 10°/min. The uncured resin obtained in (1) was subjected to a dynamic scan with a heating rate of 10°C/min from -50°C to a final temperature at which the exothermic reaction is completed and above which thermal degradation might occur. The cured epoxy resin composite on obtained in (2) was subjected to a dynamic scan with a heating rate of 10°C/min from 50°C to a final temperature at which the exothermic reaction is completed and above which thermal degradation might occur. Herein, the degree of cure can be calculated by the following formula:

$$\text{degree of cure (DoC)} = \frac{\Delta H_{\text{cured}} - \Delta H_{\text{uncured}}}{\Delta H_{\text{uncured}}} \times 100$$

where: $\Delta H_{\text{uncured}}$ = exothermic reaction peak area of an uncured resin

$\Delta H_{\text{cured}}$ = exothermic reaction peak area of a cured resin

(4) Glass transition temperature ($T_g$) of cured resin

In other embodiments of the present invention, the epoxy resin composition may have a certain $T_g$ (glass transition temperature). The $T_g$ may be determined using the following method. A specimen measuring 12.5 mm x 50 mm is cut from a cured epoxy resin composite on obtained in (2). The specimen is then subjected to measurement of $T_g$ in 1.0 Hz Torsion Mode using a dynamic viscoelasticity measuring device (ARES, manufactured by TA Instruments) by heating it to the temperatures of 50°C to 250°C at a rate of 5°C/min in accordance with SACMA SRM 18R-94. $T_g$ was determined by finding the intersect on between the tangent line of the glassy region and the tangent line of the transition region from the glassy region to the rubbery region on the temperature-elasticity modulus $G'$ curve, and the temperature at that intersect on was considered to be the glass transition temperature ($T_g$), commonly referred to as $G'$ onset $T_g$. 
(5) Water absorption

In other embodiments of the present invention, the epoxy resin composition may have a certain water absorption. Water absorption is determined using the following procedure. A specimen measuring 10 mm x 60 mm is cut from the cured epoxy resin composition obtained in (2). The specimen is immersed under boiling water for 24 hours. The water absorption can be calculated from the following formula:

\[ \text{water absorption (wt\%)} = \frac{W_i - W_B}{W_B} \times 100 \]

where: \( W_i \) = the initial weight of resin before immersion

\( W_B \) = the initial weight of resin after immersion

(6) Viscosity Measurement Method

In other embodiments of the present invention, the epoxy resin composition may have a certain viscosity at 40°C. In the present invention, "viscosity" refers to the complex viscoelastic modulus \( \eta' \).

The viscosity of the epoxy resin composition was measured using a dynamic viscoelasticity measuring device (ARES, manufactured by TA Instruments) using parallel plates with a diameter of 40 mm while increasing the temperature at a rate of 2°C/min, with a strain of 10%, frequency of 0.5 Hz, and plate interval of 1 mm, from 40°C to 130°C.

(7) Flexural Test

In other embodiments of the present invention, the epoxy resin composition may have certain flexural properties. Flexural properties were measured in accordance with the following procedure. A specimen measuring 12.5 mm x 60 mm was cut from the cured epoxy resin composition obtained in (2). Then, the specimen is processed in a 3-point bend flexural test in accordance with ASTM D7264 using an Instron Universal Testing Machine.
(manufactured by Instron). In the case of room temperature properties, the test specimens are not immersed and are tested at room temperature to obtain the RTD flexural properties of the epoxy resin composition. In the case of hot/wet properties, the specimens are immersed under boiling water for 24 hours. Then the specimens are placed in the pre-heated test chamber at 82°C and held for 3-minute prior to starting the test. The ETW flexural properties of the epoxy resin composition can be obtained from this.

(8) **Open-Hole Compression Strength (OHC) for FRP**

In some embodiments, the FRP laminate comprising the epoxy resin composition was prepared to test Open Hole Compression (OHC) strength. The prepreg was cut into 350 mm x 350 mm samples. After layering 16 sheets of the fabric prepreg samples to produce a (+45°/0° Warp/-4 5°/90° Fill)_{2s} configuration laminate, vacuum bagging was carried out, and the laminate was cured at a rate of 1.7°C/ min from room temperature to 132°C under pressure of 0.59 MPa using an autoclave to obtain a quasi-isotropic FRP material. This test specimen was then subjected to open-hole compression testing as prescribed in ASTM-D6484 using an Instron Universal Testing Machine. Measurement was taken at the elevated temperature of 82°C wet (ETW) after immersing at 71°C water for 2 weeks and at room temperature dry (RTD).

(9) **Tensile Strength (TS) for FRP**

In some embodiments, the FRP laminate comprising the epoxy resin composition was prepared to test 90° Tensile strength. The prepreg was cut into 300 mm x 300 mm samples. After laying 12 sheets of the fabric prepreg samples to produce a (90° Fill)_{12} configuration laminate and cured as described in method (8). This test specimen was then subjected to Tensile testing as prescribed in ASTM-D3039 using an Instron Universal Testing Machine. Measurement was taken at room temperature dry (RTD).
Working Examples 1-16

The various amounts of the components used for each example are stated in Tables 1 and 2. The epoxy resin compositions shown in Tables 1 and 2 were produced as described in method (1). The properties for each example are stated in Tables 1 and 2. These properties of are achieved with the cure profile described in method (2).

A prepreg comprising a reinforcing fiber impregnated with the epoxy resin composition was obtained by the following method. The epoxy resin composition obtained in method (1) was applied onto release paper using a knife coater to produce two sheets of 68.0 g/m² resin film. Next, the aforementioned two sheets of fabricated resin film were overlaid on both sides of plain weave carbon fibers (T700S-12K-50C) with a density of 1.8 g/cm² in the form of a sheet and the epoxy resin composition was impregnated using a roller temperature of 100 °C and a roller pressure of 0.07 MPa to produce a fabric prepreg with a carbon fiber areal weight of 190 g/m² and a resin content of 42wt%. The FRP material was molded as described in method (8). The TS and OHC results for some of the embodiments are stated in Tables 1 and 2.

In comparison to comparative examples 1-5, the water absorption of the epoxy resin composition in working examples 1-16 comprising the embodiments of the invention is significantly lower and heat resistance is considerably higher resulting in higher hot/wet flexural modulus.

The FRP materials were prepared by the aforementioned methods for working examples 4 and 6 comprising the embodiments of the invention. These epoxy resin compositions, in addition to providing low water absorption and high heat resistance, have significantly higher open hole compression strength particularly under hot/wet conditions as compared with comparative examples 1 and 2. In addition to the open hole compression strength improvement, the tensile strength was also
improved. This is due to the naphthalene-based epoxy resin providing high Tg and high toughness without increasing the crosslink density. It is known that lower crosslink density provides higher tensile strength. The higher tensile strength was anticipated for the working examples 4 and 6 comprising the embodiments of the invention as the crosslink density of the invention was lower than the state-of-the-art epoxy resin.
| Table 1 |
|-----------------|---------|---------|---------|---------|---------|
| **Epoxy**       | Component A | HP4770  |         |         |         |
| Component B     | MY816    |         |         |         |         |
|                  | MY965ST  | 90      | 70      | 70      | 50      |
|                  | MY0721   |         |         |         |         |
|                  | EPON828  | 10      | 30      |         |         |
|                  | GAN      |         |         |         |         |
|                  | Cel8000  |         |         |         |         |
| **Curing Agent**| Component C | Dyhard® 100S | 3 | 3 | 0 | 3 | 3 |
| Component D     | Aradur® 9664-1(4,4'-DDS) | 10 | 10 | 10 | 10 |
|                  | Aradur® 9719-1(3,3'-DDS) | | | | | |
| **Accelerators**| Component E | Dyhard® UR200 | 4 | | | |
|                  | Dyhard® UR400 | | | | | |
|                  | Omicure® U-24M | 5 | 5 | 5 | 5 |
|                  | Dyhard® URAcc13 | | | | | |
|                  | San-Aid® SI-150 | | | | | |
| **Additive**    | Thermoplastic | Sumikasecel® 5003P | 10 | 10 | 10 | 10 | 10 |
|                  | Virantage® VW-10700RFP | | | | | |
| **Epoxy Resin Properties**
- Resin viscosity at 40°C | (Pa*s) | 2,359 | 1,764 |
- Resin minimum viscosity | (Pa*s) | 4 | 6 |
- Flexural Modulus
  - RTD (GPa) | 4.1 | 3.7 |
  - ETW (GPa) | 2.9 | 2.5 | 2.9 | 2.6 | 4.0 |
- Tg
  - Dry (°C) | 142 | 148 | 100 | 150 | 162 |
  - Wet (°C) | 113 | 114 | 100 | 110 |
- Degree of Cure | (%) | 95 | 91 | 75 | 81 | 97 |
- Water absorption | (wt%) | 3.5 | 3.8 | 2.6 | 3.6 | 4.0 |
| **CFRP Properties**
- Open Hole Compression Strength | RTD (ksi) | 40 | 39 |
- Ultimate Tension strength | RTD (ksi) | 130 | 130 |

*Normalized to Vf= 48%. Note: Vf can be obtained from acid digestion test ASTM D3171-90.
### Table 2: Working Examples

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*Normalized to Vf= 48%. Note: Vf can be obtained from acid digestion test ASTM D3171-90.
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<td>155</td>
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<td>Degree of Cure</td>
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<td>96</td>
<td>97</td>
<td>98</td>
<td>96</td>
<td>96</td>
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<tr>
<td>Water absorption</td>
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<td>2.8</td>
<td>2.9</td>
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<td>2.8</td>
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<th>CFRP Properties</th>
<th>Unit</th>
<th>Ex. 9</th>
<th>Ex. 10</th>
<th>Ex. 11</th>
<th>Ex. 12</th>
<th>Ex. 13</th>
<th>Ex. 14</th>
<th>Ex. 15</th>
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<td>Ultimate Tension strength</td>
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*Normalized to VF= 48%. Note: VF can be obtained from acid digestion test ASTM D3171-90.
What is claimed is:

1. An epoxy resin composition for a fiber-reinforced composite material, comprising components (A), (B), (C), (D), and (E), wherein the epoxy resin composition has a degree of cure of at least 90% and a water absorption of at most 3.0 wt% after being cured at 132°C for 2 hours, wherein the components (A), (B), (C), (D), and (E) comprise:

   (A) at least one naphthalene-based epoxy resin having at least two naphthalene moieties and at least one glycidyl ether group per molecule;

   (B) at least one epoxy resin other than the naphthalene-based epoxy resin;

   (C) at least one dicyandiamide;

   (D) at least one diaminodiphenyl sulfone; and

   (E) at least one urea-based catalyst.

2. The epoxy resin composition according to claim 1, wherein the naphthalene-based epoxy resin is represented by Formula (1):

   ![Formula (1)](image)

   wherein n represents the number of repeating unit and is an integer of 1 or more; R₁ to R₆ are each independently selected from the group consisting of a hydrogen atom, halogen atoms, C₁ to C₆ alkyl groups, C₁ to C₆ alkoxy groups, C₁ to C₆
fluoroalkyl groups, cycloalkyl groups, aryl groups, and aryl oxyl groups where in these groups are optionally employed individually or different groups are optionally employed in combination as each of $R_1$ to $R_6$; $Y_1$ and $Y_2$ are each independently selected from the group consisting of a hydrogen atom and a glycidyl ether group wherein these groups are optionally employed individually or different groups are optionally employed in combination as each of $Y_1$ and $Y_2$; and each $X$ is independently selected from the group consisting of a direct bond, $-\text{CH}_2-$, $-\text{C(}\text{CH}_3\text{)}_2-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{O}-$, $-\text{C(=0)}\text{O}-$, $-\text{C(=0)}\text{NH}-$, $\text{C}_1$ to $\text{C}_6$ alkyl groups, $\text{C}_1$ to $\text{C}_6$ alkoxy groups, cycloalkyl groups, aryl groups and aryl oxyl groups, wherein these groups are optionally employed individually or different groups are optionally employed in combination as $X$.

3. The epoxy resin composition according to claim 1, wherein component (A) is comprised of at least one glycidyl ether of a hydroxy-substituted biphenylene selected from the group consisting of 1-(2-hydroxy-naphthalen-1-yl methyl)-naphthalene-2-ol, 1-(2-hydroxy-naphthalen-1-yl methyl)-naphthalene-2,7-diol, 1-(2-hydroxy-naphthalen-1-yl methyl)-naphthalene-7-ol, 1-(7-hydroxy-naphthalen-1-yl methyl)-naphthalene-7-ol, 1-(2,7-dihydroxy-naphthalen-1-yl methyl)-naphthalene-2,7-diol, and combinations thereof.

4. The epoxy resin composition according to claim 1, wherein component (A) is present in an amount ranging from 20 to 70phr per 100phr of total epoxy resin.

5. The epoxy resin composition according to claim 1, wherein component (B) is comprised of a component (Bl) and a component (B2) which are different from each other.

6. The epoxy resin composition according to claim 5, wherein the component (Bl) comprises an epoxy resin having more than two epoxy-functional groups per molecule.
7. The epoxy resin composition according to claim 6, wherein component (Bl) is present in an amount ranging from 30 to 80 phr per 100 phr of total epoxy resin.

8. The epoxy resin composition according to claim 5, wherein the component (B2) comprises an epoxy resin having less than three epoxy-functional groups per molecule.

9. The epoxy resin composition according to claim 8, wherein the epoxy resin has an epoxy equivalent weight of less than 205 g/eq.

10. The epoxy resin composition according to claim 8, wherein the epoxy resin has an epoxy equivalent weight of less than 170 g/eq.

11. The epoxy resin composition according to claim 8, wherein component (B2) is present in an amount of at most 30 phr per 100 phr of total epoxy resin.

12. The epoxy resin composition according to claim 1, wherein component (B) comprises at least one tetraglycidylamine epoxy resin.

13. The epoxy resin composition according to claim 5, wherein component (Bl) comprises at least one tetraglycidylamine epoxy resin and component (B2) comprises at least one epoxy resin selected from the group consisting of bisphenol A epoxy resins, diglycidylamine, and cycloaliphatic epoxy resins.

14. The epoxy resin composition according to claim 1, wherein component (C) is present in an amount ranging from 2 to 7 phr per 100 phr of total epoxy resin.

15. The epoxy resin composition according to claim 1, wherein component (D) is present in an amount ranging from 5 to 30 phr per 100 phr of total epoxy resin.

16. The epoxy resin composition according to claim 1, wherein component (E) comprises at least one aromatic urea catalyst.
17. The epoxy resin composition according to claim 1, wherein component (E) comprises at least one urea-based catalyst selected from the group consisting of N,N-dimethyl-N'-(3, 4-dichlorophenyl) urea, toluene bis(dimethyl urea), 4,4'-(methylen bis(phenyl dimethyl urea), N-(4-chlorophenyl) N,N-dimethyl urea and 3-phenyl-1, 1-dimethyl urea.

18. The epoxy resin composition according to claim 1, wherein component (E) is present in an amount ranging from 1 to 8 phr per loophr of total epoxy resin.

19. The epoxy resin composition according to claim 1, wherein the epoxy resin composition when cured at 132°C for two hours has a hot/wet flexural modulus of at least 3.0 GPa.

20. The epoxy resin composition according to claim 1, wherein the epoxy resin composition when cured at 132°C for two hours has a hot/wet glass transition temperature of at least 115°C.

21. The epoxy resin composition according to claim 1, wherein the epoxy resin composition further comprises at least one thermoplastic resin.

22. The epoxy resin composition according to claim 5, wherein the epoxy resin comprising the component (B2) has a viscosity at 40°C in the range of 1 x 10^3 to 3 x 10^4 Pa-s.

23. The epoxy resin composition according to claim 1, wherein components (A), (B), (C) and (D) are each present in an amount effective to provide a molar ratio of active hydrogens:epoxy groups of from 0.4:1 to 0.8:1.

24. A prepreg, comprising a reinforcing fiber matrix impregnated with an epoxy resin composition in accordance with any one of claims 1 to 23.

25. A fiber-reinforced composite material obtained by curing a prepreg in accordance with claim 24.

26. A fiber-reinforced composite material, comprising a cured epoxy resin product obtained by curing a mixture comprised
of an epoxy resin composition in accordance with any one of claims 1 to 23 and a reinforcing fiber.

27. A method of making a fiber-reinforced composite material, comprising curing a prepreg in accordance with claim 24 at a temperature of from 110°C to 150°C.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

Int.Cl. C08G59/56 (2006.01)i, C08L63/00 (2006.01)i

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C08G59/56, C08L63/00

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

- Published examined utility model applications of Japan 1992-1996
- Published unexamined utility model applications of Japan 1971-2017
- Registered utility model specifications of Japan 1996-2017
- Published registered utility model applications of Japan 1994-2017

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>JP 2013-166917 A (TORAY INDUSTRIES, INC.)</td>
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<td>2013.08.29, Claims, [0016]-[0048], [0073], [0081], Examples (No family)</td>
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<td>JP 2003-26768 A (TORAY INDUSTRIES, INC.) 2003.01.29, [0030] (No family)</td>
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* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier application or patent but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "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
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  - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - "&" document member of the same patent family

**Date of the actual completion of the international search**

**Date of mailing of the international search report**

10.08.2017

22.08.2017

Name and mailing address of the ISA/JP

**Japan Patent Office**

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