

Description

Title of Invention:

EPOXY RESIN COMPOSITION FOR FIBER-REINFORCED COMPOSITE
MATERIAL, PREPREG, AND FIBER-REINFORCED COMPOSITE
5 MATERIAL

Technical Field

[0001]

The present invention relates to an epoxy resin composition for a fiber-
10 reinforced composite material, a prepreg, and a fiber-reinforced composite
material.

Background Art

[0002]

15 Epoxy resins have traditionally been the mainstream as matrix resins for
carbon fibers and glass fiber-reinforced composite materials (FRPs) applied to
aircraft and the like, and are applied to many of body structures. For example,
Patent Document 1 describes an epoxy resin composition containing an epoxy
resin as a matrix, a thermoplastic resin for viscosity adjustment, a filler, and a
20 curing agent, and also describes a prepreg obtained by combining the
composition and a reinforcing fiber.

[0003]

Heat resistance requirements of the aircraft are determined according to
the site, and are roughly classified into, for example, approximately 95°C (or
25 higher) and approximately 70°C. Blending of the epoxy resin composition
corresponding to these requirements can be classified into blending through
curing at 180°C and blending through curing at 120°C, and 180°C-cured
products and 120°C-cured products are obtained at the curing temperatures.

[0004]

30 On the other hand, it has been pointed out that FRP requires a high
manufacturing cost. Especially, a process of curing and molding a prepreg by
an autoclave through use of machine or hand lay-up requires high costs for
many auxiliary materials used for bagging before curing, high autoclave
equipment management cost, and high energy cost, and such high costs are
35 considered to be the main factors to raise the manufacturing cost. Therefore,
investigation and development of methods for manufacturing an FRP without
using a prepreg or autoclave, such as filament winding (FW) and resin transfer
(RTM) molding methods, have also been actively made. However, in terms of

quality reproducibility and reliability of manufactured parts, it has not been possible to achieve a level equal to or higher than that of the hand lay-up-autoclave prepreg molding method. The manufacturing cost when using an autoclave increases in proportion to the curing temperature, pressure, and time.

5 Therefore, when a prepreg material that can be cured at as a low temperature and a low pressure as possible can be applied, the cost for manufacturing by an autoclave, which is currently the most reliable, can be reduced. For example, when the process currently divided into curing at 120°C and curing at 180°C can be unified into curing at 120°C curing on a low temperature side, the
10 efficiency of curing by an autoclave can be improved, which can contribute greatly to reduction of the manufacturing cost.

Citation List

Patent Literature

15 [0005]

Patent Document 1: JP 2011-099094 A

Summary of Invention

Technical Problem

20 [0006]

An object of the present invention is to provide an epoxy resin composition for a fiber-reinforced composite material, a prepreg, and a fiber-reinforced composite material, which can be molded at a low temperature and a low pressure, have sufficient heat resistance and mechanical properties for
25 practical use, and enable significant reduction of manufacturing costs.

Solution to Problem

[0007]

As a result of diligent research, the present inventors have found that the
30 above problems can be solved by a resin composition obtained by blending specific amounts of (a) one or more epoxy resins, (b) an aromatic diamine compound, (c) a dicyandiamide, (d) a urea compound, and (e) an amine adduct compound, and have completed the present invention.

[0008]

35 The present invention provides an epoxy resin composition for a fiber-reinforced composite material, including: (a) one or more epoxy resins; (b) an aromatic diamine compound; (c) a dicyandiamide; (d) a urea compound; and (e) an amine adduct compound, blended in the following blending proportions:

a blending proportion of the (b) aromatic diamine compound being from 0.2 to 0.6 equivalents relative to the (a) epoxy resin,

a blending proportion of the (c) dicyandiamide being from 0.5 to 4.0 mass% relative to a total of the (a) to (e) components,

5 a blending proportion of the (d) urea compound being from 0.5 to 2.0 mass% relative to the total of the (a) to (e) components, and

a blending proportion of the (e) amine adduct compound being 0 to 3.0 mass% relative to the total of the (a) to (e) components.

10 Advantageous Effects of Invention

[0009]

The epoxy resin composition for a fiber-reinforced composite material (hereinafter, simply referred to as resin composition) according to an embodiment of the present invention includes (a) one or more epoxy resins, (b) 15 an aromatic diamine compound, (c) a dicyandiamide, (d) a urea compound, and (e) an amine adduct compound, blended in specific amounts, and thus can be molded at a low temperature and a low pressure, has sufficient heat resistance and mechanical properties for practical use, and enables significant reduction of a manufacturing cost.

20 In particular, for the resin composition according to an embodiment of the present invention, the process currently divided into curing at 120°C and curing at 180°C can be unified into curing at 120°C on a low temperature side. For example, when the prepreg in an embodiment of the present invention is cured by an autoclave under low temperature/low pressure conditions (for 25 example, at 120°C, for 90 minutes, and at 0.31 MPa), FRPs having heat resistance and mechanical properties equivalent to those of 120°C-cured products of the prior art can be obtained. It is also possible to obtain FRPs having heat resistance and mechanical properties equivalent to those of 180°C-cured products of the prior art by subjecting the cured products to post-curing 30 (e.g., at 180°C, for 2 hours, and at atmospheric pressure). The post-curing does not require pressurization using an autoclave, and, for example, only heat may be applied using an air-circulating oven or the like. Therefore, when 180°C-cured products are manufactured, auxiliary materials required at the time of curing at 180°C by an autoclave are also unnecessary, and the manufacturing 35 cost when an autoclave is used can be reduced. In addition, at the time of post-curing, products can be demolded from a layering jig and heated in a free-standing state, and thus improvement in productivity due to shortening of a mold occupancy time can be achieved. According to the prepreg in an

embodiment of the present invention, 180°C-cured products can be manufactured using an autoclave. Also in this case, cured products having molding quality, heat resistance, and mechanical properties equivalent to those of 180°C-cured products of the prior art can be obtained.

5 As further described above, in accordance with the present invention, in a case where a 120°C-cured product is manufactured and also in a case where a 180°C-cured product is manufactured, a 120°C-cured product can be manufactured first. Thus, it is unnecessary to provide materials corresponding to the cured products as in the prior art, and also to store and manage the cured
10 products, and the manufacturing cost can be reduced.

From the above, the present invention can provide an epoxy resin composition for a fiber-reinforced composite material, a prepreg, and a fiber-reinforced composite material, which can be molded at a low temperature and a low pressure, have sufficient heat resistance and mechanical properties for
15 practical use, and enable significant reduction of manufacturing costs.

Description of Embodiments

[0010]

The present invention will be described in further detail below.

20 The epoxy resin composition according to an embodiment of the present invention includes: (a) one or more epoxy resins; (b) an aromatic diamine compound; (c) a dicyandiamide; (d) a urea compound; and (e) an amine adduct compound, blended in the following blending proportions:

a blending proportion of the (b) aromatic diamine compound being from
25 0.2 to 0.6 equivalents relative to the (a) epoxy resin,

a blending proportion of the (c) dicyandiamide being from 0.5 to 4.0 mass% relative to a total of the (a) to (e) components,

a blending proportion of the (d) urea compound being from 0.5 to 2.0 mass% relative to the total of the (a) to (e) components, and

30 a blending proportion of the (e) amine adduct compound being 0 to 3.0 mass% relative to the total of the (a) to (e) components.

[0011]

(a) Epoxy resin

In a suitable form, all of the (a) epoxy resins can be composed of
35 trifunctional or higher functional epoxy resins. Alternatively, a bifunctional epoxy resin may be used in combination as the (a) epoxy resins. In this case, the (a) epoxy resins are preferably composed of: from 0 to 80 mass% of a

bifunctional epoxy resin; and from 20 to 100 mass% of a trifunctional or higher functional epoxy resin.

[0012]

Examples of the trifunctional or higher functional epoxy resin include
5 polyfunctional type glycidyl ether epoxy resins such as phenol novolac type, orthocresol novolac type, trishydroxyphenylmethane type, and tetraphenylolthane type, and glycidylamine epoxy resins such as a tetraglycidyl-diaminodiphenylmethane, tetraglycidyl-m-xylylenediamine, triglycidyl-p-aminophenol, and triglycidyl-m-aminophenol.

10 [0013]

The trifunctional or higher functional epoxy resin is preferably a liquid or semi-solid epoxy resin from the perspective of having higher heat resistance, more appropriate viscosity, and excellent workability (for example, impregnation property into a fiber base material).

15 A single trifunctional or higher functional epoxy resin can be used, or two or more trifunctional or higher functional epoxy resins can be used in combination.

[0014]

Examples of the bifunctional epoxy resin include epoxy compounds with
20 bisphenol groups, such as bisphenol A type, bisphenol F type, brominated bisphenol A type, hydrogenated bisphenol A type, bisphenol S type, bisphenol AF type, and biphenyl type; polyalkylene glycol type and alkylene glycol type epoxy compounds; epoxy compounds with naphthalene rings; and epoxy compounds with fluorene groups.

25 A single bifunctional epoxy resin can be used, or two or more bifunctional epoxy resins can be used in combination.

[0015]

(b) Aromatic diamine compound

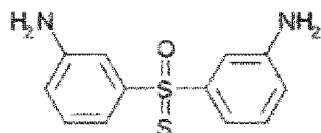
The (b) aromatic diamine compound has an effect of curing the (a)
30 epoxy resin. The (b) aromatic diamine compound used in an embodiment of the present invention is not particularly limited as long as it has the effect described above, but is preferably one or more selected from the group consisting of 3,3'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfone, 4,4'-methylenebis(2,6-diethylaniline) and 4,4'-methylenebis(2-ethyl-6-
35 methyl)benzeneamine, from the perspective of improving the effects of the present invention.

[0016]

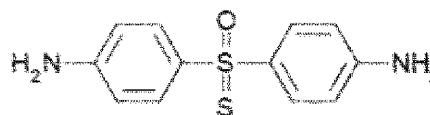
Structures of these suitable (b) aromatic diamine compounds will be shown below.

[0017]

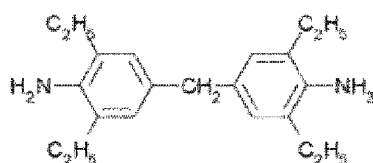
[Chemical Formula 1]



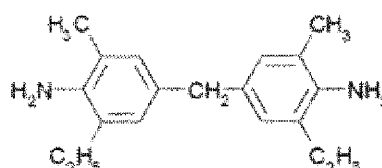
3,3'-Diaminodiphenylsulfone



4,4'-Diaminodiphenylsulfone



4,4'-Methylenebis(2,6-diethylaniline)



4,4'-Methylenebis(2-ethyl-6-methyl)benzeneamine

[0018]

In the resin composition according to an embodiment of the present invention, the blending proportion of the (b) aromatic diamine compound is from 0.2 to 0.6 equivalents relative to the (a) epoxy resin. When the blending proportion falls outside the range, heat resistance deteriorates. A preferred blending proportion of the (b) aromatic diamine compound is from 0.3 to 0.5 equivalents relative to the (a) epoxy resin.

[0019]

(c) Dicyandiamide

The (c) dicyandiamide has the effect of curing the (a) epoxy resin and has the following structure.

[0020]

[Chemical Formula 2]



Dicyandiamide

[0021]

In the resin composition according to an embodiment of the present invention, the blending proportion of the (c) dicyandiamide is from 0.5 to 4.0 mass% relative to the total of the (a) to (e) components. When the blending proportion falls outside this range, heat resistance deteriorates, or curability at

low temperatures, such as 120°C, deteriorates. A preferred blending proportion of the (c) dicyandiamide is from 1.0 to 3.0 mass% relative to the total of the (a) to (e) components.

[0022]

5 (d) Urea compound

The (d) urea compound has an effect of promoting a curing reaction of the (a) epoxy resin. The (d) urea compound used in an embodiment of the present invention is not particularly limited as long as it has the effect described above, but is preferably one or more selected from the group

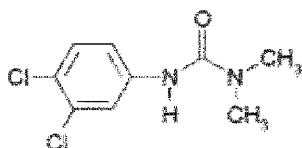
10 consisting of 3-(3,4'-dichlorophenyl)-1,1-dimethylurea, 2,4-toluenebisdimethylurea, and 4,4'-methylenebis(phenyldimethylurea).

[0023]

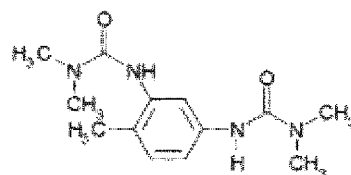
Structures of these suitable (d) urea compounds will be shown below.

[0024]

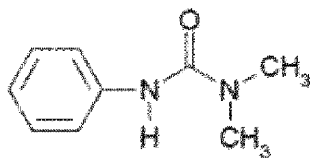
15 [Chemical Formula 3]



3-(3,4'-Dichlorophenyl)-1,1-dimethylurea



2, 4-Toluenebisdimethylurea



4,4'-Methylenebis(phenyldimethylurea)

[0025]

In the resin composition according to an embodiment of the present invention, the blending proportion of the (d) urea compound is from 0.5 to 2.0 mass% relative to the total of the (a) to (e) components. When the blending proportion falls outside this range, heat resistance or curability deteriorates. A preferred blending proportion of the (d) urea compound is from 0.5 to 1.5 mass% relative to the total of the (a) to (e) components.

25 [0026]

(e) Amine adduct compound

The (e) amine adduct compound has the effect of promoting the curing reaction of the (a) epoxy resin. The (e) amine adduct compound is an adduct of

an amine, such as an adduct of an amine and at least one compound selected from the group consisting of an epoxy resin, an isocyanate compound, and a urea compound.

[0027]

5 The amine may have, for example, one or more active hydrogens capable of performing an addition reaction with an epoxy group, a phenol group, or an isocyanate group in one molecule, and have one or more of at least one selected from the group consisting of a primary amino group, a secondary amino group, and a tertiary amino in one molecule. Specific examples of the
10 amine include 2-methylimidazole, N-methylimidazole, 2-ethyl-4-methylimidazole, N-methylpiperazine, 2,4,6-tris(dimethylaminomethyl)phenol, 2-dimethylaminoethanol, 2-undecylimidazolol, 2-phenylimidazole, and 2-octadecylimidazole.

[0028]

15 The epoxy resin is not particularly limited. Examples of the epoxy resin include polyglycidyl ethers obtained by reacting a polyhydric phenol such as bisphenol A, bisphenol F, bisphenol AD, catechol, or resorcinol, or a polyhydric alcohol such as glycerin or polyethylene glycol with epichlorohydrin; glycidyl ether esters obtained by reacting a hydroxycarboxylic
20 acid such as p-hydroxybenzoic acid or β -hydroxynaphthoic acid with epichlorohydrin; polyglycidyl esters obtained by reacting a polycarboxylic acid such as phthalic acid or terephthalic acid with epichlorohydrin; epoxidized phenol novolac resins, epoxidized cresol novolac resins, epoxidized polyolefins, cyclic aliphatic epoxy resins, urethane-modified epoxy resins, and
25 glycidylamine type epoxy resins obtained from 4,4 diaminodiphenylmethane, m-aminophenol, or the like.

[0029]

 The isocyanate compound is not particularly limited. Examples of the isocyanate compound include monofunctional isocyanate compounds such as n-
30 butyl isocyanate, phenyl isocyanate, and hexamethylene diisocyanate; and polyfunctional compounds such as hexamethylene diisocyanate, toluylene diisocyanate, 1,5-naphthalene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and 1,3,6-hexamethylene triisocyanate.

[0030]

35 The urea compound is not particularly limited as long as it is a compound having at least one selected from the group consisting of a ureido bond, a urethane bond, and NH-CO-N. Examples of the urea compound include

urea, urea phosphate, urea oxalate, urea acetate, diacetyl urea, dibenzoyl urea, and trimethyl urea.

[0031]

In the resin composition according to an embodiment of the present invention, the blending proportion of the (e) amine adduct compound is from 0 to 3.0 mass% relative to the total of the (a) to (e) components. When the blending proportion of the (e) amine adduct compound is greater than 3.0 mass%, the balance in curability of the resin is lost, and the low-temperature curability at 120°C deteriorates, or the heat resistance of the cured product worsens. A preferred blending proportion of the (e) amine adduct compound is from 0 to 2 mass% relative to the total of the (a) to (e) components.

The resin composition according to an embodiment of the present invention may additionally contain an additive depending on an intended use without departing from the object of the present invention. Examples of components that can be added include flame retardants, thermoplastic resins and rubbers for improving toughness of cured resins, and inorganic particles for controlling resin fluidity and improving resin rigidity during curing.

[0032]

The resin composition according to an embodiment of the present invention has excellent curability. For example, the resin composition can be cured under the curing conditions: at 120°C and for 1.5 hours, until a state where it can be demolded from the mold. The obtained cured product has a glass transition temperature of 110°C or higher, and has high heat resistance. The resin composition according to an embodiment of the present invention has a reaction start temperature (exothermic peak onset temperature) of 90°C or higher and 120°C or lower according to differential scanning calorimetry (DSC analysis) at a temperature increase rate of 10°C/min, and thus curing at 120°C reliably proceeds.

Note that the glass transition temperature referred to herein is measured by thermomechanical analysis (TMA), and specific conditions for the analysis are as follows.

Device used: TMA 4000S Thermomechanical Analyzer available from Bruker AXS

Temperature increase rate: 10°C/min

Measurement mode: expansion mode

Load applied: 2 g

Measurement atmosphere: air

Specific conditions for the DSC analysis are as follows.

Device used: DSC2500 Differential Scanning Calorimeter available from TA Instruments

Temperature increase rate: 10°C/min

Measurement atmosphere: nitrogen gas

5 [0033]

In addition, in an embodiment of the present invention, a cured product having heat resistance and mechanical properties equivalent to those of 180°C-cured products of the prior art can be formed by subjecting the cured product to post-curing (for example, at 180°C, for 2 hours, and atmospheric pressure). The
10 post-curing does not require pressurization using an autoclave, and, for example, only heat may be applied using an air-circulating oven or the like. Therefore, auxiliary materials required at the time of curing at 180°C by an autoclave are also unnecessary, and the manufacturing cost when an autoclave is used can be reduced. In addition, at the time of post-curing, products can be
15 demolded from a layering jig and heated in a free-standing state, and thus improvement in productivity due to shortening of a mold occupancy time can be achieved.

The cured product after this post-curing has a glass transition temperature of 180°C or higher, and has high heat resistance.

20 [0034]

The prepreg according to an embodiment of the present invention is obtained using the resin composition according to an embodiment of the present invention and a fiber base material.

Specifically, the prepreg according to an embodiment of the present
25 invention is obtained by impregnating the resin composition according to an embodiment of the present invention into a fiber base material.

The fiber base material used in the prepreg according to an embodiment of the present invention is not particularly limited, but, for example, is preferably any of glass fiber, quartz fiber, aramid fiber, or carbon fiber.
30 Examples of a form of the fiber base material include woven fabrics, roving, nonwoven fabrics, knit fabrics, and tulle.

A method for manufacturing the prepreg according to an embodiment of the present invention is not particularly limited. Examples of the method include dipping methods using a solvent and hot melt methods (solvent-free
35 methods).

[0035]

The fiber-reinforced composite material according to an embodiment of the present invention is a cured product of the prepreg according to an

embodiment of the present invention. An intended use of the fiber-reinforced composite material according to an embodiment of the present invention is not particularly limited, and examples thereof include aircraft parts (e.g., radomes, fairings, flaps, leading edges, floor panels, propellers, fuselages, and the like);
5 two-wheel vehicle parts (e.g., motorcycle frames, cowls, fenders, and the like); automobile parts (e.g., doors, bonnets, tailgates, side fenders, side panels, fenders, energy absorbers, trunk lids, hard tops, side mirror covers, spoilers, diffusers, ski carriers, engine cylinder covers, engine hoods, chassis, air spoilers, propeller shafts, and the like); vehicle exterior plating (e.g., lead car
10 noses, roofs, side panels, doors, truck bed covers, side skirts, and the like); railroad vehicle parts (e.g., luggage racks, seats, and the like); aero parts (e.g., side skirts and the like mounted on automobiles and rigid vehicles such as interior design elements, inner panels, outer panels, roofs, and floors of wings on wing trucks, and the like); use as housings (e.g., notebook computers,
15 portable phones, and the like); medical uses (e.g., X-ray cassettes, table tops, and the like); audio product uses (e.g., flat speaker panels, speaker cones, and the like); sports goods uses (e.g., golf club heads, face masks, snowboards, surf boards, protectors, and the like); and general industrial uses (e.g., flat springs, windmill blades, and elevators (compartment panels, doors).

20

Example

[0036]

The present invention will be described in further detail by way of examples and comparative examples, but the present invention is not limited by
25 these examples.

[0037]

Examples 1 to 4 and Comparative Examples 1 to 8

In the examples and comparative examples, the following materials were
used.

30

(a) Epoxy resin

- Trifunctional or higher functional epoxy resin (YH-404 available from NIPPON STEEL Chemical & Material Co., Ltd., epoxy equivalent = 115)
- Trifunctional or higher functional epoxy resin (MY-0510 available
35 from Huntsman Advanced Material, epoxy equivalent = 101)
- Trifunctional or higher functional epoxy resin (VG3101L available from Printech co., ltd., epoxy equivalent = 210)

- Bifunctional epoxy resin (YD-128 available from NIPPON STEEL Chemical & Material Co., Ltd., epoxy equivalent = 191)

- Bifunctional epoxy resin (HP-4032SS available from DIC Corporation, epoxy equivalent = 143)

5 • Bifunctional epoxy resin (EpoxyMKS35K available from Printech co., ltd., epoxy equivalent = 962)

[0038]

(b) Aromatic diamine

10 • 4,4'-Diaminodiphenylsulfone (available from Wakayama Seika Kogyo Co., Ltd.)

[0039]

(c) Dicyandiamide

15 • Dicyandiamide (Dicy15 available from Mitsubishi Chemical Corporation)

[0040]

(d) Urea compound

20 • 4,4'-Methylenebis(phenyl dimethylurea) (Omicure U-24M available from CVC Thermoset Specialities)

[0041]

(e) Amine adduct compound

25 • Amine-epoxy adduct compound (PN-40J available from Ajinomoto Fine-Techno Co., Inc.)

[0042]

30 According to the blending proportions (parts by mass) listed in Table 1 below, the materials were kneaded by using a kneader, and thus each resin composition was prepared.

[0043]

35 Next, the prepared resin composition was poured into a die having dimensions of 200 mm × 200 mm × 3 mm, and then heated under conditions: at 120°C and for 1.5 hours, and a 120°C-cured product was attempted to be manufactured. Table 1 shows whether curing is possible, the appearance of the resultant cured product, and the glass transition temperature thereof. Note that a part of the resin cured product was cut into approximately 3 mm square, and that the glass transition temperature was measured by the method described above.

Next, the 120°C-cured product was subjected to post-curing at 180°C for 3 hours, and a 180°C-cured product was manufactured. Note that this post-curing was performed by heating the resin cured product under atmospheric

pressure using an air-circulating oven in a free-standing state without using a die. The appearance and glass transition temperature of the resultant cured product were examined.

The results are shown in Table 1.

5 [0044]

The following mechanical properties were measured for the 120°C-cured product and the 180°C-cured product obtained above.

[0045]

- Tensile strength (measured in accordance with ASTM D638)
- 10 • Tensile elastic modulus (measured in accordance with ASTM D638)
- Tensile elongation (measured in accordance with ASTM D638)
- Bending strength (measured in accordance with ASTM D790)
- Bending elastic modulus (measured in accordance with ASTM D790)
- Bending elongation (measured in accordance with ASTM D790)
- 15 • Tensile toughness (calculated from load-strain curve in tensile test)
- Bending toughness (calculated from load-strain curve in bending test)

[0046]

The results are shown in Table 2.

20

[0047]

[Table 1]

Blended Components	Product name	Equivalent	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 7	Comparative Example 8	
(a)	YH-404	115	40	70	60	35	100	0	60	100	60
Trifunctional or higher functional epoxy resin	MY-0510	101	0	0	0	30	0	0	0	0	0
	VG3101L	210	30	0	0	0	0	0	0	0	0
	YD-128	191	30	0	0	0	0	100	0	0	0
(a) Bifunctional epoxy resin	HP-4032SS	143	0	30	30	30	0	0	0	0	30
	EpoxMKSR35K	962	0	0	10	5	0	0	0	0	10
Trifunctional or higher functional epoxy/bifunctional epoxy ratio	0	0	70/30	70/30	60/40	65/35	100/0	0/100	60/40	100/0	60/40
(b) Aromatic diamine compound	4,4'-DDS	63	16.3	25.8	18.7	20.6	38.3	23.1	21.9	32.9	32.7

(c)	Dicy15	-	2.0	1.0	2.0	2.0	2.0	0.0	5.0	2.0	2.0	2.0	2.0	1.0
Dicyandiamide														1.0
(d) Urea compound	OmicureU-24M	-	1.0	1.0	1.0	1.0	1.0	0.0	1.0	0.0	0.0	1.0	1.0	1.0
(e) Amine adduct compound	PN-40J	-	1.0	1.0	1.0	1.0	0.0	0.0	1.0	2.0	3.0	1.0	9.9	1.0
Blending total		(phr)	120.3	128.8	122.7	123.6	138.3	123.1	121.0	125.9	126.9	104.0	142.8	135.7
(b) Equivalent ratio	Equivalent ratio relative to (a)		0.4	0.5	0.4	0.4	0.7	0.7	0.3	0.4	0.4	0.0	0.6	0.7
(c) Blending proportion	wt.% relative to total of (a) to (e)		1.66	0.78	1.63	1.62	0.00	0.00	4.13	1.59	1.58	1.92	0.00	0.74
(d) Blending proportion	wt.% relative to total of (a) to (e)		0.83	0.78	0.82	0.81	0.00	0.00	0.83	0.00	0.00	0.96	0.00	0.74
(e) Blending proportion	wt.% relative to total of (a) to (e)		0.83	0.78	0.82	0.00	0.00	0.00	0.83	1.59	2.36	0.96	6.94	0.74
Reaction temperature	Start temperature	°C	98	96	90	104	154	132	105	94	88	110	98	100
(DSC exothermic peak)	Onset temperature	°C	124	146	124	132	203	179	129	153	116	147	124	151
Cured state	120°C-cured product	Whether curing is possible	Possible	Possible	Possible	Possible	Not possible	Not possible	Possible	Not possible	Not possible	Possible	Not possible	Possible

	120°C-cured product	Appearance	Transparent		Slightly cloudy						Slightly suspended	Slightly suspended	Possible	Possible	Uncured in center portion
	180°C-cured product	Whether curing is possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible
	180°C-cured product	Appearance	Transparent		Slightly cloudy		Transparent	Transparent			Slightly suspended	Slightly suspended	Uneven when deforming		
Glass transition temperature	120°C-cured product	°C	135	118	138	136	-	-	118	-	-	108	48	115	
	180°C-cured product	°C	189	182	182	183	220	115	156	205	204	161	166	134	

[0048]

[Table 2]

Item	Unit	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Tensile strength	120°C-cured product	59	64	70	80	0	0	71
Tensile elastic modulus	120°C-cured product	4.0	4.1	4.1	4.1	0.0	0.0	4.1
Tensile elongation	120°C-cured product	1.7	1.7	1.9	2.3			2.0

Tensile strength	180°C-cured product	(MPa)	31	53	42	41	43	45	42
Tensile elastic modulus	180°C-cured product	[GPa]	3.2	3.5	3.5	3.5	4.0	4.0	3.6
Tensile elongation	180°C-cured product	(%)	1.0	1.7	1.3	1.3	1.2	1.2	1.3
Bending strength	120°C-cured product	(MPa)	139	167	157	162	0	0	182
Bending elastic modulus	120°C-cured product	[GPa]	3.9	4.3	4.1	4.2			4.2
Bending elongation	120°C-cured product	(%)	4.1	4.4	4.6	4.5	0.0	0.0	5.7
Bending strength	180°C-cured product	(MPa)	113	158	148	153	151	167	159
Bending elastic modulus	180°C-cured product	[GPa]	3.3	3.5	3.5	3.4	3.8	4.0	3.7
Bending elongation	180°C-cured product	(%)	4.0	5.9	5.5	6.4	4.8	6.1	6.0
Tensile toughness	120°C-cured product	[kgf-mm/mm ²]	1546	1224	2152	4146	0	0	1835
	180°C-cured product	[kgf-mm/mm ²]	371	1055	651	748	744	842	692

Bending toughness	120°C-cured product	[kgf-mm/mm ²]	1126	1302	1343	1337	0	0	1844
	180°C-cured product	[kgf-mm/mm ²]	870	1768	1511	1963	1312	2153	1699

[0049]

From the results shown in Tables 1 and 2, it was confirmed that, in each of the examples, the resin composition was well cured at 120°C, and that the resultant cured product also had sufficient heat resistance and mechanical properties for practical use. Furthermore, it was confirmed that the 180°C-cured product obtained by subjecting the 120°C-cured product to post-curing at 180°C also had sufficient heat resistance and mechanical properties for practical use.

In contrast, in Comparative Examples 1 and 2, neither the (c) dicyandiamide nor the (d) urea compound, according to an embodiment of the present invention, was blended, and thus curing at 180°C could be confirmed, but curing at 120°C could not be confirmed.

In Comparative Example 3, the blending proportion of the (c) component exceeded the upper limit specified in an embodiment of the present invention, and thus the heat resistance of the 180°C-cured product worsened.

Only the degree of curing was confirmed in Comparative Examples 4 to 8, and the results are shown in Table 1.

Claims

1. An epoxy resin composition for a fiber-reinforced composite material, comprising:
 - (a) one or more epoxy resins;
 - (b) an aromatic diamine compound;
 - (c) a dicyandiamide;
 - (d) a urea compound; and
 - (e) an amine adduct compound,blended in the following blending proportions:
 - a blending proportion of the (b) aromatic diamine compound being from 0.2 to 0.6 equivalents relative to the (a) epoxy resin,
 - a blending proportion of the (c) dicyandiamide being from 0.5 to 4.0 mass% relative to a total of the (a) to (e) components,
 - a blending proportion of the (d) urea compound being from 0.5 to 2.0 mass% relative to the total of the (a) to (e) components, and
 - a blending proportion of the (e) amine adduct compound being 0 to 3.0 mass% relative to the total of the (a) to (e) components.
2. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein a glass transition temperature of a cured product is 110°C or higher, the cured product being obtained by curing the resin composition under curing conditions: at 120°C and for 1.5 hours, until a state where demolding from a mold can be performed.
3. The epoxy resin composition for a fiber-reinforced composite material according to claim 2, wherein the cured product has a glass transition temperature of 180°C or higher by post-curing at 180°C for 2 hours.
4. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the (a) epoxy resin comprises from 0 to 80 mass% of a bifunctional epoxy resin and from 20 to 100 mass% of a trifunctional or higher functional epoxy resin.
5. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein a reaction start temperature (exothermic peak onset temperature) according to differential scanning calorimetry (DSC

analysis) at a temperature increase rate of 10°C/min is 90°C or higher and 120°C or lower.

6. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the (b) aromatic diamine compound is one or more selected from the group consisting of 3,3'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfone, 4,4'-methylenebis(2,6-diethylaniline) and 4,4'-methylenebis(2-ethyl-6-methyl)benzeneamine.
7. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the (d) urea compound is one or more selected from the group consisting of 3-(3,4'-dichlorophenyl)-1,1-dimethylurea, 2,4-toluenebisdimethylurea, and 4,4'-methylenebis(phenyldimethylurea).
8. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the blending proportion of the (b) aromatic diamine compound is from 0.3 to 0.5 equivalents relative to the (a) epoxy resin.
9. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the blending proportion of the (c) dicyandiamide is from 1.0 to 3.0 mass% relative to the total of the (a) to (e) components.
10. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the blending proportion of the (d) urea compound is from 0.5 to 1.5 mass% relative to the total of the (a) to (e) components.
11. The epoxy resin composition for a fiber-reinforced composite material according to claim 1, wherein the blending proportion of the (e) amine adduct compound is from 0 to 2 mass% relative to the total of the (a) to (e) components.
12. A prepreg comprising the epoxy resin composition for a fiber-reinforced composite material according to claim 1, the epoxy resin composition being impregnated into any of glass fiber, quartz fiber, aramid fiber, or carbon fiber.
13. A fiber-reinforced composite material, which is a cured product of the prepreg according to claim 12.