

DESCRIPTION

TITLE OF INVENTION: EPOXY RESIN, CURABLE RESIN COMPOSITION, CURED PRODUCTS THEREOF, AND CARBON FIBER-REINFORCED COMPOSITE

MATERIAL

5 TECHNICAL FIELD

[0001] The present invention relates to an epoxy resin, a curable resin composition, a cured product thereof, and a carbon fiber-reinforced composite material.

BACKGROUND ART

[0002] By curing epoxy resins with various curing agents, the epoxy resins become cured
10 products with excellent mechanical properties, water resistance, chemical resistance, heat resistance, electrical properties, etc., and are used in a wide range of fields such as adhesives, paints, laminates, molding materials, and casting materials. Carbon fiber-reinforced composite materials (CFRPs) made by impregnating and curing reinforcement fibers with epoxy resins and curing agents as matrix resins can be given properties such as light weight and high
15 strength, and therefore have been widely deployed in recent years in aircraft structural members, wind turbine blades, automobile exterior panels, and computer applications such as IC trays and notebook computer housings, and demand for them is increasing. In particular, they are used as matrix resins for aircraft applications, taking advantage of the light weight and high strength properties of the molded bodies.

20 [0003] Thermosetting resin cured products such as epoxy resins used as resins in matrix resins such as CFRP are generally brittle, but high mechanical strength is required when applied to structural materials for aerospace and vehicles. To compensate for the low flexural strength, toughness, adhesiveness, etc. of this thermosetting resin, a method of adding a highly tough thermoplastic resin to the thermosetting resin matrix is widely known (Patent
25 Literatures 1 to 3). Specifically, the flexural strength and toughness of the prepreg are improved by combining particles of thermoplastic resins such as polyethersulfone,

polyetherimide, and polyamide with the thermosetting resin matrix resin.

[0004] In recent years, the properties required for CFRP have become stricter, and resins with superior heat resistance are required, particularly when used in aerospace applications and as structural materials for vehicles, etc. (Patent Literature 4).

5 CITATION LIST

PATENT LITERATURE

[0005]

Patent Literature 1: Japanese Patent Application Publication No. S60(1985)-243113

Patent Literature 2: Japanese Patent Application Publication No. H09(1997)-100358

10 Patent Literature 3: Japanese Patent Application Publication No. 2013-155330

Patent Literature 4: Japanese Patent Application Publication No. 2010-275492

Patent Literature 5: Japanese Patent Application Publication No. 2007-211254

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

15 [0006] A low water-absorbent epoxy resin is described in Patent Literature 5. However, the epoxy resin described in Patent Literature 5 has low heat resistance, and is difficult to use as a CFRP material.

[0007] The present invention has been made in consideration of the above circumstances, and an object of the present invention is to provide an epoxy resin, a curable resin

20 composition, and a cured product thereof, and a carbon fiber-reinforced composite material, all of which have excellent heat resistance.

SOLUTION TO PROBLEM

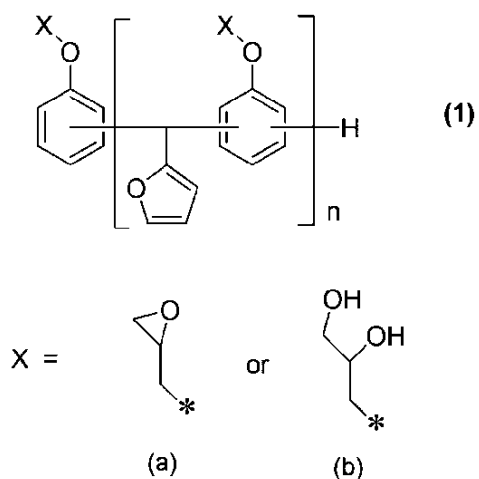
[0008] That is, the present invention relates to the following [1] to [6]. In the present invention, "(Numerical value 1) to (Numerical value 2)" indicates that the upper and lower

25 limits are included.

[1] An epoxy resin represented by the following formula (1), wherein a ratio b/a is 0.012

or more and 0.050 or less, in which “a” is a peak area of a compound represented by the following formula (2) in a chromatogram of high performance liquid chromatography of the epoxy resin, and “b” is a peak area of a compound represented by the following formula (3) in the chromatogram.

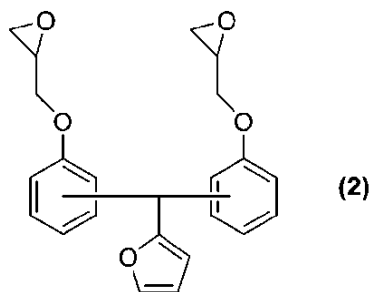
5 [0009] [Chem. 1]



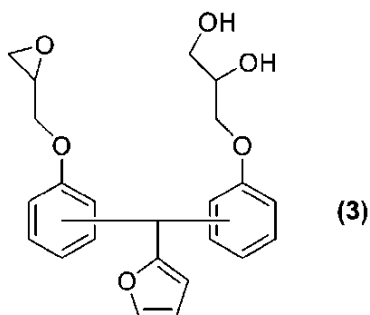
[0010] In formula (1), n is an average number of repeats and is a real number in the range of $1 < n < 15$. Each X is independently a monovalent group represented by formula (a) or formula (b), and at least one X is a monovalent group represented by formula (a). * binds to an oxygen atom.

10

[0011] [Chem. 2]



[0012] [Chem. 3]



[0013]

[2] The epoxy resin according to the preceding [1], having an epoxy equivalent of 200 g/eq. or more and 220 g/eq. or less.

5 [3] A curable resin composition containing the epoxy resin according to the preceding [1] or [2] and a curing agent.

[4] The curable resin composition according to the preceding [3], wherein the curing agent is an amine-based curing agent.

[5] A cured product obtained by curing the curable resin composition according to the
10 preceding [3] or [4].

[6] A carbon fiber-reinforced composite material obtained by curing the curable resin composition according to the preceding [3] or [4].

ADVANTAGEOUS EFFECTS OF INVENTION

[0014] According to the present invention, it is possible to provide an epoxy resin, a curable
15 resin composition, and a cured product thereof, and a carbon fiber-reinforced composite material, the cured product of which has excellent heat resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0015]

[Figure 1] is a HPLC chart of Synthesis Example 1.

20 [Figure 2] is a HPLC chart of Synthesis Example 2.

[Figure 3] is a HPLC chart of Synthesis Example 3.

[Figure 4] is a HPLC chart of Synthesis Example 4.

[Figure 5] is a HPLC chart of Synthesis Example 5.

[Figure 6] is a HPLC chart of Synthesis Example 6.

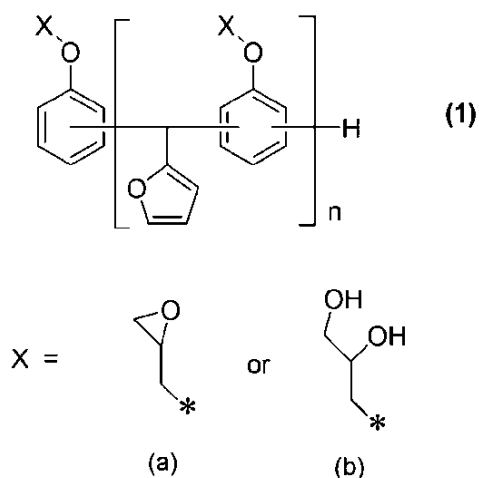
[Figure 7] is a HPLC chart of Synthesis Example 7.

5 DESCRIPTION OF EMBODIMENTS

[0016] Hereinafter, an embodiment of the present invention (hereinafter, also referred to as "the present embodiment") will be described in further detail.

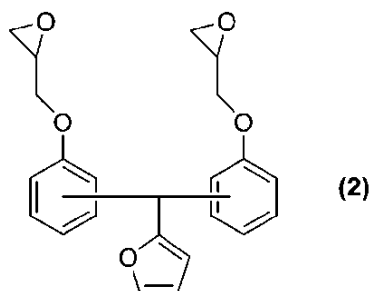
[0017] The epoxy resin of the present invention is represented by the following formula (1), in which, b/a is 0.012 or more and 0.050 or less, in which "a" is a peak area of a compound represented by the following formula (2) in a chromatogram of high performance liquid chromatography of the epoxy resin, and "b" is a peak area of a compound represented by the following formula (3) in the chromatograph.

[0018] [Chem. 4]

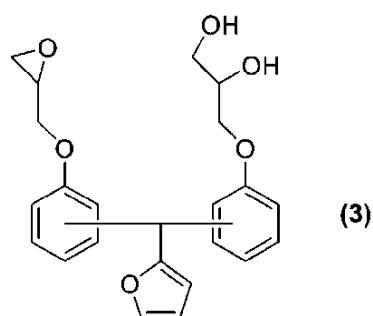


[0019] In formula (1), n is an average number of repetitions and is a real number satisfying $1 < n < 15$. Each X is independently a monovalent group represented by formula (a) or formula (b), and at least one X is a monovalent group represented by formula (a). * binds to an oxygen atom.

[0020] [Chem. 5]



[0021] [Chem. 6]



[0022] In the formula (1), the value of n can be calculated from a number average molecular weight of the epoxy resin measured by gel permeation chromatography (GPC, detector: RI) or the area ratio of each of the separated peaks. n is preferably a real number of $1 < n < 15$, more preferably $1 < n < 10$, and particularly preferably $1 < n < 5$.

[0023] The epoxy resin of the present embodiment can obtain a cured product with excellent heat resistance by controlling the value of b/a . Specifically, it is preferable that b/a is 0.012 or more and 0.050 or less, more preferably 0.014 or more and 0.040 or less, and even more preferably 0.015 or more and 0.030 or less. The reason why the heat resistance is good when b/a is 0.12 or more is not clearly understood, but it is thought that the molecules become difficult to move due to the influence of hydrogen bonds when a certain amount of the compound represented by the formula (3) is contained. When b/a is greater than 0.050, the amount of the compound represented by the formula (3) increases, and the crosslinking points during curing are reduced, so the glass transition point (T_g) decreases. In the present embodiment, HPLC (high performance liquid chromatography) is measured by the method

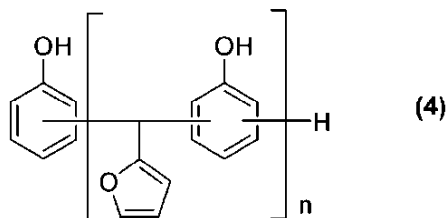
described in the Examples below.

[0024] The glass transition point (T_g) of the epoxy resin of the present embodiment is preferably 170 to 300°C, more preferably 172 to 250°C, and even more preferably 174 to 200°C. If the glass transition point is less than 170°C, it is difficult to apply the resin to components that require heat resistance, such as those around an aircraft engine, and the resin softens during use, significantly reducing the mechanical strength, which is undesirable as it can lead to damage to the material. In addition, the glass transition point of an epoxy resin generally correlates with the crosslink density, and the higher the crosslink density, the higher the glass transition point. In other words, if the glass transition point exceeds 300°C, the crosslink density increases and the mechanical strength of the cured product becomes brittle, which is undesirable. The glass transition point (T_g) of the present embodiment is measured by the method described in the Examples below.

[0025] The epoxy equivalent of the epoxy resin of the present embodiment is preferably 200 g/eq. or more and 220 g/eq. or less, more preferably 204 g/eq. or more and 218 g/eq. or less, and even more preferably 213 g/eq. or more and 218 g/eq. or less.

[0026] The epoxy resin represented by the formula (1) can be obtained by reacting a phenolic resin represented by the following formula (4) with epihalohydrin.

[0027] [Chem. 7]



[0028] In formula (4), n is the average number of repetitions and is a real number satisfying $1 < n < 15$.

[0029] The preferred range of n in the formula (4) is the same as that in the formula (1).

[0030] The epihalohydrin is readily available on the market. The amount of epihalohydrin

used is preferably 2.0 to 10 mol, more preferably 3.0 to 8.0 mol, and even more preferably 3.5 to 6.0 mol, per mol of hydroxy group of the phenolic resin represented by formula (4).

Preferred examples of epihalohydrin that can be used in the present embodiment include epichlorohydrin, α -methylepichlorohydrin, β -methylepichlorohydrin, epibromohydrin, and the like, and epichlorohydrin, which is easily available industrially, is particularly preferred.

[0031] In the above reaction, an alkali metal hydroxide can be used as a catalyst for accelerating the epoxidation step. Examples of alkali metal hydroxides that can be used include sodium hydroxide and potassium hydroxide. A solid alkali metal hydroxide may be used, or an aqueous solution of an alkali metal hydroxide may be used. In the present embodiment, it is particularly preferable to use a solid alkali metal hydroxide molded into a flake shape in terms of solubility and handling. The amount of the alkali metal hydroxide used is preferably 0.90 to 1.5 mol, more preferably 0.95 to 1.25 mol, and even more preferably 0.99 to 1.15 mol, per mol of hydroxy groups of the phenolic resin represented by formula (4).

[0032] In order to promote the reaction, a quaternary ammonium salt such as tetramethylammonium chloride, tetramethylammonium bromide, trimethylbenzylammonium chloride, etc. may be added as a catalyst. The amount of the quaternary ammonium salt used is preferably 0.1 to 15 g, more preferably 0.2 to 10 g, per mole of hydroxy group of the phenolic resin represented by formula (4).

[0033] The reaction temperature is preferably 30 to 90°C, more preferably 35 to 80°C. In particular, in the present embodiment, for higher purity epoxidation, a temperature of 50°C or higher is preferred, and particularly 60°C or higher is preferred. The reaction time is preferably 0.5 to 10 hours, more preferably 1 to 8 hours, and particularly preferably 1 to 3 hours. If the reaction time is too short, the reaction will not proceed to completion, and if the reaction time is too long, by-products will be produced, which is undesirable.

[0034] The reaction product of these epoxidation reactions (mixture A containing the epoxy resin represented by the above formula (1)) can be washed with water, or without washing

with water, and then epihalohydrin, solvent, and the like are removed from the reaction product under reduced pressure with heating to obtain mixture B containing the epoxy resin represented by the above formula (1). Mixture B contains the epoxy resin represented by the above formula (1), a trace amount of residual solvent, and by-product salt. Furthermore, in order to obtain an epoxy resin with a smaller amount of hydrolyzable halogen, mixture B is dissolved in a ketone compound having 4 to 7 carbon atoms (e.g., methyl isobutyl ketone, methyl ethyl ketone, cyclopentanone, cyclohexanone, etc.) or an aromatic hydrocarbon compound having 6 to 10 carbon atoms (e.g., toluene, xylene, etc.) as a solvent, and an aqueous solution of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide is added to carry out the reaction. In Patent Literature 5, the reaction is carried out by adding only an aqueous solution of an alkali metal hydroxide, but in the present embodiment, water and/or alcohol is further added to the aqueous solution of the alkali metal hydroxide to carry out the reaction. As a result, a compound represented by the above formula (3) is produced, and it has been found that this can improve heat resistance. The amount of alkali metal hydroxide used is preferably 0.01 to 0.3 moles, preferably 0.05 to 0.2 moles, per mole of hydroxy group of the phenolic resin represented by formula (4) used in the epoxidation. The amount of water used is 10 to 40% by weight, preferably 15 to 25% by weight, based on the theoretical yield of the epoxy resin represented by formula (1). Examples of alcohol include methanol, ethanol, propanol, and isopropanol. The amount of alcohol used is 5 to 40% by weight, preferably 15 to 25% by weight, based on the theoretical yield of the epoxy resin represented by formula (1). The total amount of water and alcohol used is 15 to 60% by weight, preferably 20 to 50% by weight, based on the theoretical yield of the epoxy resin represented by formula (1). The reaction temperature is preferably 50 to 120°C, and the reaction time is more preferably 0.5 to 2 hours.

[0035] After the reaction is completed, the produced salt is removed by filtration, washing with water, or the like, and the solvent is further distilled off under reduced pressure with

heating to obtain the epoxy resin of the present embodiment.

[0036] In the synthesis method of the phenolic resin represented by the formula (4) above, when furfural is reacted (condensed) with phenols, the amount of the phenols is preferably 1.5 to 20 moles, particularly preferably 3 to 10 moles, per mole of furfural.

5 [0037] Examples of the phenols include: disubstituted phenols such as catechol, resorcinol, and hydroquinone; and monosubstituted phenols such as phenol, cresol, and xlenol. These may be used alone or in combination of two or more kinds.

[0038] Solvents used in the synthesis of phenolic resins include, but are not limited to, methanol, ethanol, propanol, isopropanol, toluene, xylene, etc., and may be used alone or in
10 combination of two or more. When a solvent is used, the amount of the solvent used is preferably 5 to 500 parts by weight, more preferably 10 to 300 parts by weight, based on 100 parts by weight of the phenols.

[0039] In the condensation reaction of furfural and phenols, it is preferable to use a base catalyst. Although condensation polymerization is possible with an acid catalyst, the reaction
15 between furfurals also occurs, resulting in a large amount of by-products. There is also a method of using an organometallic compound as a catalyst, but this is disadvantageous in terms of cost. Specific examples of basic catalysts include: alkali metal hydroxides such as lithium hydroxide, sodium hydroxide, and potassium hydroxide; alkaline earth metal hydroxides such as magnesium hydroxide and calcium hydroxide; alkali metal alkoxides such
20 as sodium methoxide, sodium ethoxide, potassium methoxide, potassium ethoxide, and potassium-tert-butoxide; and alkaline earth metal alkoxides such as magnesium methoxide and magnesium ethoxide, but the present invention is not limited to these, and these catalysts may be used alone or in combination of two or more kinds. The amount of catalyst used is preferably 0.005 to 2.0 moles, more preferably 0.01 to 1.1 moles, per 1 mole of the hydroxy
25 group of the phenols.

[0040] The condensation reaction in the presence of these base catalysts is preferably carried

out in the range of 40 to 180°C, particularly preferably in the range of 80 to 165°C. The time for the condensation reaction can be selected in the range of 0.5 to 10 hours. The system is neutralized so that the system becomes neutral, or the reaction product thus obtained is repeatedly washed with water in the presence of a solvent and then the water is separated and drained, and the solvent and unreacted materials are removed under reduced pressure with heating to obtain the phenolic resin represented by the formula (4).

[0041] The curable resin composition of the present embodiment contains a curing agent. Examples of the curing agent that can be used include an amine-based curing agent, an acid anhydride-based curing agent, an amide-based curing agent, and a phenol-based curing agent.

[0042] In the curable resin composition of the present embodiment, an amine-based curing agent is preferred, since it is possible to achieve a good balance between the resin viscosity of the curable resin composition and the heat resistance of the cured resin. Examples of amine-based curing agents include 3,3'-diaminodiphenyl sulfone (3,3'-DDS), 4,4'-diaminodiphenyl sulfone (4,4'-DDS), diaminodiphenylmethane (DDM), 3,3'-diisopropyl-4,4'-diaminodiphenylmethane, 3,3'-di-*t*-butyl-4,4'-diaminodiphenylmethane, 3,3'-diethyl-5,5'-dimethyl-4,4'-diaminodiphenylmethane, 3,3'-diisopropyl-5,5'-dimethyl-4,4'-diaminodiphenylmethane, 3,3'-di-*t*-butyl-5,5'-dimethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (TEDDM), 3,3'-diisopropyl-5,5'-diethyl-4,4'-diaminodiphenylmethane, 3,3'-di-*t*-butyl-5,5'-diethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane, 3,3'-di-*t*-butyl-5,5'-diisopropyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetra-*t*-butyl-4,4'-diaminodiphenylmethane, diaminodiphenyl ether (DADPE), bisaniline, benzyldimethylaniline, 2-(dimethylaminomethyl)phenol (DMP-10), 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30), 2-ethylhexanoate ester of 2,4,6-tris(dimethylaminomethyl)phenol, and the like can be used.

Other examples include aniline novolak, orthoethylaniline novolak, aniline resins obtained by reacting aniline with xylylene chloride, and aniline resins obtained by polycondensation of

aniline with substituted biphenyls (4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, etc.) or substituted phenyls (1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene, 1,4-bis(hydroxymethyl)benzene, etc.).

- 5 [0043] Examples of the acid anhydride curing agent include phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methyl nadic anhydride, hexahydrophthalic anhydride, and methylhexahydrophthalic anhydride.
- [0044] Examples of the amide-based curing agent include dicyandiamide, or a polyamide
10 resin synthesized from a dimer of linoleic acid and ethylenediamine.
- [0045] Examples of phenol-based curing agents include polyhydric phenols (bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, terpene diphenol, 4,4'-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, 3,3',5,5'-tetramethyl-(1,1'-biphenyl)-4,4'-diol, hydroquinone, resorcin, naphthalene diol, tris-(4-hydroxyphenyl)methane, and 1,1,2,2-tetrakis(4-
15 hydroxyphenyl)ethane, etc.); phenolic resins obtained by condensation of phenols (e.g., phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, and dihydroxynaphthalene, etc.) with aldehydes (formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde and furfural), ketones (p-hydroxyacetophenone, o-hydroxyacetophenone, etc.), or dienes (dicyclopentadiene,
20 tricyclopentadiene, etc.); phenolic resins obtained by condensation of the above-mentioned phenols with substituted biphenyls (4,4'-bis(chloromethyl)-1,1'-biphenyl and 4,4'-bis(methoxymethyl)-1,1'-biphenyl, etc.) or substituted phenyls (1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene and 1,4-bis(hydroxymethyl)benzene, etc.); modified products of the above-mentioned phenols and/or
25 the above-mentioned phenolic resins; and halogenated phenols such as tetrabromobisphenol A and brominated phenolic resins.

[0046] In the curable resin composition of the present embodiment, it is also preferable to use the phenolic resin represented by the formula (4) as the entire amount of the curing agent or as a part thereof.

[0047] In the curable resin composition of the present embodiment, the amount of the curing agent used is preferably 0.7 to 1.2 equivalents relative to 1 equivalent of the epoxy group of the epoxy resin. If the amount is less than 0.7 equivalents or if the amount exceeds 1.2 equivalents relative to 1 equivalent of the epoxy group, curing may be incomplete and good cured physical properties may not be obtained.

[0048] In addition, in the curable resin composition of the present embodiment, a curing accelerator may be blended as necessary. The gelation time can also be adjusted by using a curing accelerator. Examples of curing accelerators that can be used include: imidazoles such as 2-methylimidazole, 2-ethylimidazole, and 2-ethyl-4-methylimidazole; tertiary amines such as 2-(dimethylaminomethyl)phenol and 1,8-diaza-bicyclo[5,4,0]undecene-7; phosphines such as triphenylphosphine; and metal compounds such as tin octylate. The curing accelerator is used in an amount of 0.01 to 5.0 parts by weight per 100 parts by weight of the epoxy resin as necessary.

[0049] In the curable resin composition of the present embodiment, other epoxy resins may be blended. Specific examples thereof include: polycondensation products of phenols (phenol, alkyl-substituted phenol, aromatic substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted dihydroxybenzene, dihydroxynaphthalene, etc.) and various aldehydes (formaldehyde, acetaldehyde, alkyl aldehyde, benzaldehyde, alkyl-substituted benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde, crotonaldehyde, cinnamaldehyde, etc.); polycondensation products of phenols and various diene compounds (dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, etc.); polycondensation products of phenols and

ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, etc.); phenolic resins obtained by polycondensation of phenols and substituted biphenyls (4,4'-bis(chloromethyl)-1,1'-biphenyl and 4,4'-bis(methoxymethyl)-1,1'-biphenyl, etc.) or substituted phenyls (1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene, 1,4-bis(hydroxymethyl)benzene, etc.); polycondensates of bisphenols and various aldehydes; glycidyl ether epoxy resins obtained by glycidylating alcohols; alicyclic epoxy resins such as 4-vinyl-1-cyclohexene diepoxide and 3,4-epoxycyclohexylmethyl-3,4'-epoxycyclohexanecarboxylate; glycidyl amine epoxy resins such as tetraglycidyl diamine diphenylmethane (TGDDM) and triglycidyl-p-aminophenol; glycidyl ester epoxy resins, etc., but are not limited thereto, so long as they are commonly used epoxy resins.

[0050] The curable resin composition of the present embodiment can be mixed with known additives as necessary. Specific examples of additives that can be used include polybutadiene and its modified products, modified products of acrylonitrile copolymers, polyphenylene ether, polystyrene, polyethylene, polyimide, fluororesin, maleimide-based compounds, cyanate ester-based compounds, silicone gel, silicone oil; and inorganic fillers such as silica, alumina, calcium carbonate, quartz powder, aluminum powder, graphite, talc, clay, iron oxide, titanium oxide, aluminum nitride, asbestos, mica, and glass powder; surface treatment agents for fillers such as silane coupling agents; release agents; and colorants such as carbon black, phthalocyanine blue, and phthalocyanine green.

[0051] The curable resin composition of the present embodiment may contain a known maleimide compound as necessary. Specific examples of the maleimide compound that may be used include 4,4'-diphenylmethane bismaleimide, polyphenylmethane maleimide, m-phenylene bismaleimide, 2,2'-bis[4-(4-maleimidophenoxy)phenyl]propane, 3,3'-dimethyl-5,5'-diethyl-4,4'-diphenylmethane bismaleimide, 4-methyl-1,3-phenylene bismaleimide, 4,4'-diphenylether bismaleimide, 4,4'-diphenylsulfone bismaleimide, 1,3-bis(3-

maleimidophenoxy)benzene, 1,3-bis(4-maleimidophenoxy)benzene, and biphenylalkyl maleimide, but are not limited thereto. These may be used alone or in combination of two or more. When the maleimide compound is blended, a curing accelerator is blended if necessary. The above-mentioned curing accelerators, as well as radical polymerization initiators such as organic peroxides and azo compounds can be used.

[0052] The curable resin composition of the present embodiment can be made into a varnish-like composition (hereinafter, simply referred to as varnish) by adding an organic solvent. Examples of the solvent to be used include: amide-based solvents such as γ -butyrolactones, N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylimidazolidinone; sulfones such as tetramethylene sulfone; ether-based solvents such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol, propylene glycol monomethyl ether, propylene glycol monomethyl ether monoacetate, and propylene glycol monobutyl ether; ketone-based solvents such as methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone, and cyclohexanone; and aromatic solvents such as toluene and xylene. The solvent is used in such a range that the solids concentration excluding the solvent in the obtained varnish is preferably 10 to 80% by weight, more preferably 20 to 70% by weight.

[0053] The curable resin composition of the present embodiment can also be used as a resin sheet, a prepreg, or a carbon fiber-reinforced composite material.

The curable resin composition of the present embodiment may be applied to one or both sides of a support substrate and used as a resin sheet. Examples of application methods include a casting method, a method of extruding a resin from a nozzle or a die using a pump or an extruder, and adjusting the thickness with a blade, a method of adjusting the thickness by calendaring with a roll, and a method of spraying using a spray or the like. In addition, in the step of forming a layer, the curable resin composition may be heated in a temperature range that can avoid thermal decomposition. In addition, rolling treatment, grinding treatment,

etc. may be performed as necessary. Examples of support substrates include, but are not limited to: porous substrates made of paper, cloth, nonwoven fabric, etc.; plastic films or sheets such as polyethylene, polypropylene, polyethylene terephthalate, and polyester films; nets, foams, metal foils, and appropriate thin bodies such as laminates thereof. The thickness of the support substrate is not particularly limited and is appropriately determined depending on the application.

[0054] The curable resin composition and/or resin sheet of the present embodiment can be heated and melted to reduce the viscosity, and then impregnated into a fiber substrate to obtain the prepreg of the present embodiment.

[0055] The prepreg of the present embodiment can also be obtained by impregnating a fiber substrate with the varnish-like curable resin composition and drying it by heating. The prepreg is cut into a desired shape, laminated, and then the laminate is heated and cured while applying pressure by press molding, autoclave molding, sheet winding molding, or the like, to obtain the carbon fiber-reinforced composite material of the present embodiment. Copper foil or an organic film can also be laminated when laminating the prepreg.

[0056] Furthermore, the carbon fiber-reinforced composite material of the present embodiment can be obtained by molding using a known method other than the above-mentioned method. For example, a resin transfer molding technique (RTM method) can be used in which a carbon fiber substrate (usually a carbon fiber fabric) is cut, laminated, and shaped to produce a preform (a preform before being impregnated with resin), the preform is placed in a mold, the mold is closed, resin is injected to impregnate the preform, the resin is hardened, and the mold is opened to remove the molded product.

Also usable are a type of RTM method, such as the VaRTM method, the Seeman's Composite Resin Infusion Molding Process (SCRIMP) method, and the Controlled Atmospheric Pressure Resin Infusion (CAPRI) method, which is described in Japanese Patent Publication No. 2005-527410, in which a resin supply tank is evacuated to a pressure lower

than atmospheric pressure, circulation compression is used, and the net molding pressure is controlled to more appropriately control the resin injection process, particularly the VaRTM method.

[0057] Further, a film stacking method in which a fiber substrate is sandwiched between resin sheets (films), a method in which a powdered resin is attached to a reinforcing fiber substrate to improve impregnation, a molding method (Powder Impregnated Yarn) in which a fluidized bed or fluid slurry method is used in the process of mixing the resin into the fiber substrate, and a method in which resin fibers are mixed into the fiber substrate can also be used.

[0058] Examples of carbon fibers include acrylic, pitch, and rayon carbon fibers. Among them, acrylic carbon fibers having high tensile strength are preferably used. As the form of carbon fibers, twisted yarn, untwisted yarn, non-twisted yarn, etc. can be used, but untwisted yarn or non-twisted yarn is preferably used because it has a good balance between the formability and strength properties of the fiber-reinforced composite material.

Examples

[0059] The present invention will be described in more detail below with reference to synthesis examples and examples. The materials, processing contents, processing procedures, etc. shown below can be appropriately changed without departing from the spirit of the present invention. Therefore, the scope of the present invention should not be interpreted as being limited by the specific examples shown below.

[0060] The analysis was performed under the following conditions.

Hydroxy equivalent

Hydroxy equivalent is
measured by the following method, in g/eq.

The phenolic resin was reacted with excess acetic anhydride, and titrated with 0.5N KOH ethanol solution using a potentiometer to measure the amount of free acetic acid.

Reagents: acetic anhydride, triphenylphosphine, pyridine

Solvent: tetrahydrofuran, propylene glycol monomethyl ether

Automatic titrator: COM-1600 manufactured by HIRANUMA Corporation

Burette: B-2000 manufactured by HIRANUMA Corporation

5 Epoxy equivalent was m

Epoxy equivalent was measured by the method described in JIS K-7236, in g/eq.

HPLC (High Performance Liquid Chromatography)

Shimadzu Corporation Liquid Delivery Unit LC-20AD

Shimadzu Corporation Photodiode Array Detector SPD-M20A

10 Shimadzu Corporation Column Oven CTO-20A

Column: Intersil ODS-2.5 μ m, 4.6 $\times$ 250mm, 40 $^{\circ}$ C

Mobile Phase A: Acetonitrile (AN)

Mobile Phase B: Water (W)

15 Gradient elution was performed to give a gradient to the composition of the mobile phase as follows.

Time Program:

From 0 minutes to 28 minutes from the start, the ratio AN/W of mobile phase A to mobile phase B was changed from 50%/50% to 100%/0%.

20 From 28 minutes to 40 minutes from the start, the ratio AN/W of mobile phase A to mobile phase B was set to 100%/0%.

The flow rate of the mobile phase was 1.0 mL/min.

Ultraviolet rays with a wavelength of 274 nm were detected by a photodiode array (PDA) that detects ultraviolet rays with wavelengths of 200 nm to 274 nm.

GPC (gel permeation chromatography) analysis

25 Device: ACQUITY APC system (manufactured by Waters)

Column: Guard column SHODEX GPC KF-601, KF-602 KF-602.5, KF-603

Flow rate: 0.5 ml/min.

Column temperature: 40°C

Solvent used: THF (tetrahydrofuran)

Detector: RI (differential refractometer)

5 [0061] [Synthesis Example 1]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a heating device. After stirring and dissolving, the mixture was heated to 110°C, and 33 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C
10 for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. Immediately after reaching 145°C, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to
15 obtain 90 parts by weight of the phenolic resin represented by the formula (4). The hydroxy equivalent of the obtained phenolic resin was 141 g/eq. 78 parts by weight of the obtained phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of epichlorohydrin (ECH, hereinafter the same), 64 parts by weight of dimethyl sulfoxide (DMSO, hereinafter the same), and 13 parts by weight of water, and the
20 mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was charged in portions over 2 hours while maintaining the temperature of the solution at 45°C. Then, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60 minutes. Then, the mixture was repeatedly washed with water to remove by-product salts and dimethyl sulfoxide, and excess epichlorohydrin was distilled off
25 from the oil layer under reduced pressure with heating to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The

theoretical yield of the epoxy resin in this reaction is 109 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 22 parts by weight of water, 22 parts by weight of methanol, and 7 parts by weight of 30% aqueous sodium hydroxide solution were added and reacted for 1 hour. The reaction solution was then repeatedly washed with water until the washing solution became neutral. Then, 107 parts by weight of the epoxy resin represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under reduced pressure with heating (n in formula (1) is 1.7). The epoxy equivalent of the obtained epoxy resin was 204 g/eq. The HPLC results are shown in Figure 1. The peaks of the compound represented by the formula (2) were at 13.5 minutes, 14.2 minutes, and 15.3 minutes, and the peaks of the compound represented by the formula (3) were at 10.5 minutes, 11.3 minutes, and 11.6 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6 minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.015.

[0062] [Synthesis Example 2]

In a flask equipped with a stirrer, a reflux condenser, and a heating device, 254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged, stirred, dissolved, and heated to 110°C, and 53 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. After reaching 145°C, the mixture was reacted for 4 hours. Then, the mixture was cooled to 80°C, 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 109 parts by weight of the phenolic resin represented by the formula (4). The hydroxy equivalent of the obtained phenolic resin was 142 g/eq. 78 parts by weight of the obtained

phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of ECH, 64 parts by weight of DMSO, and 13 parts by weight of water, and the mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was charged in portions over 2 hours while maintaining the temperature of the solution at 45°C. Then, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60 minutes. After repeated washing with water to remove by-product salts and dimethyl sulfoxide, excess epichlorohydrin was distilled off from the oil layer under reduced pressure with heating to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The theoretical yield of the epoxy resin in this reaction is 109 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 22 parts by weight of water, 22 parts by weight of methanol, and 7 parts by weight of 30% aqueous sodium hydroxide solution were added and reacted for 1 hour. The reaction solution was then repeatedly washed with water until the washing solution became neutral. Then, 103 parts by weight of the epoxy resin represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under reduced pressure with heating (n in formula (1) is 2.0). The epoxy equivalent of the obtained epoxy resin was 214 g/eq. The HPLC results are shown in Figure 2. The peaks of the compound represented by the formula (2) were at 13.5 minutes, 14.2 minutes, and 15.3 minutes, and the peaks of the compound represented by the formula (3) were at 10.5 minutes, 11.3 minutes, and 11.6 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6 minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.015.

[0063] [Synthesis Example 3]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a

heating device, and after stirring and dissolving, the mixture was heated to 110°C, and 63 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. Immediately after reaching 145°C, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 112 parts by weight of the phenolic resin represented by the above formula (4). The hydroxy group equivalent of the obtained phenolic resin was 147 g/eq. 78 parts by weight of the obtained phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of epichlorohydrin (ECH, hereinafter the same), 64 parts by weight of dimethyl sulfoxide (DMSO, hereinafter the same), and 13 parts by weight of water, and the mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was charged in portions over 2 hours while maintaining the temperature of the solution at 45°C. Then, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60 minutes. Then, the mixture was repeatedly washed with water to remove by-product salts and dimethyl sulfoxide, and excess epichlorohydrin was distilled off from the oil layer under heating and reduced pressure to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The theoretical yield of the epoxy resin in this reaction is 108 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 22 parts by weight of water, 22 parts by weight of methanol, and 7 parts by weight of 30% aqueous sodium hydroxide solution were added and reacted for 1 hour. The reaction solution was then repeatedly washed with water until the washing solution became neutral. Then, 103 parts by

weight of the epoxy resin represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under heating and reduced pressure (n in formula (1) is 2.2). The epoxy equivalent of the obtained epoxy resin was 218 g/eq. The HPLC results are shown in Figure 3. The peaks of the compound represented by the formula (2) were at 13.7 minutes, 14.4 minutes, and 15.5 minutes, and the peaks of the compound represented by the formula (3) were at 10.7 minutes, 11.5 minutes, and 11.8 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6 minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.017.

[0064] [Synthesis Example 4]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a heating device, and after stirring and dissolving, the mixture was heated to 110°C, and 53 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. After reaching 145°C, the mixture was reacted for 4 hours. Then, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize the mixture. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 109 parts by weight of the phenolic resin represented by the formula (4). The hydroxy equivalent of the obtained phenolic resin was 142 g/eq. 78 parts by weight of the obtained phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of ECH, 64 parts by weight of DMSO, and 13 parts by weight of water, and the mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was charged in portions over 2 hours while maintaining the temperature of the solution at 45°C. Then, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60

minutes. After repeated washing with water to remove by-product salts and dimethyl sulfoxide, excess epichlorohydrin was distilled off from the oil layer under reduced pressure with heating to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The theoretical yield of the epoxy resin in this reaction is 109 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 22 parts by weight of water, 26 parts by weight of methanol, and 7 parts by weight of 30% aqueous sodium hydroxide solution were added and reacted for 1 hour. The reaction solution was then repeatedly washed with water until the washing solution became neutral. Then, 101 parts by weight of the epoxy resin represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under reduced pressure with heating (n in formula (1) is 2.1). The epoxy equivalent of the obtained epoxy resin was 213 g/eq. The HPLC results are shown in Figure 4. The peaks of the compound represented by the formula (2) were at 13.5 minutes, 14.2 minutes, and 15.3 minutes, and the peaks of the compound represented by the formula (3) were at 10.5 minutes, 11.3 minutes, and 11.6 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6 minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.026.

[0065] [Synthesis Example 5]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a heating device, and after stirring and dissolving, the mixture was heated to 110°C, and 44 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. Immediately after reaching 145°C, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of

phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize.

After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 109 parts by weight of the phenolic resin represented by the formula

(4). The hydroxy equivalent of the obtained phenolic resin was 142 g/eq. 78 parts by weight

5 of the obtained phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of ECH, 64 parts by weight of DMSO, and 13 parts by weight of water, and the mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was charged in portions over 2 hours while maintaining the temperature of the solution at 45°C. Then, the reaction was further carried out
10 at 45°C for 2 hours and at 70°C for 60 minutes. After repeated washing with water to remove by-product salts and dimethyl sulfoxide, excess epichlorohydrin was distilled off from the oil layer under reduced pressure with heating to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The theoretical yield of the epoxy resin in this reaction is 109 parts by weight.

15 218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 5 parts by weight of water and 7 parts by weight of 30% aqueous sodium hydroxide solution were added, and the reaction solution was reacted for 1 hour. The reaction solution was repeatedly washed with water until the washing solution became neutral. Then, 103 parts by weight of the epoxy resin
20 represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under reduced pressure with heating (n in formula (1) is 1.8). The epoxy equivalent of the obtained epoxy resin was 207 g/eq.

The HPLC results are shown in Figure 5. The peaks of the compound represented by the formula (2) were at 13.5 minutes, 14.2 minutes, and 15.3 minutes, and the peaks of the
25 compound represented by the formula (3) were at 10.5 minutes, 11.3 minutes, and 11.6 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6

minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.009.

[0066] [Synthesis Example 6]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a heating device, and after stirring and dissolving, the mixture was heated to 110°C, and 40 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. After reaching 145°C, the mixture was reacted for 4 hours. Then, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize the mixture. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 107 parts by weight of the phenolic resin represented by the formula (4). The hydroxy equivalent of the obtained phenolic resin was 141 g/eq. 78 parts by weight of the obtained phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of ECH, 64 parts by weight of DMSO, and 13 parts by weight of water, and the mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was gradually added to the flask over 2 hours while maintaining the temperature of the reaction solution at 45°C. Then, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60 minutes. After repeated washing with water to remove by-product salts and dimethyl sulfoxide, excess epichlorohydrin was distilled off from the oil layer under reduced pressure with heating to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The theoretical yield of the epoxy resin in this reaction is 109 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained

mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 5 parts by weight of water and 7 parts by weight of 30% aqueous sodium hydroxide solution were added, and the reaction solution was reacted for 1 hour. The reaction solution was repeatedly washed with water until the washing solution became neutral. Then, 90 parts by weight of the epoxy resin represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under reduced pressure with heating (n in formula (1) is 2.0). The epoxy equivalent of the obtained epoxy resin was 211 g/eq.

The HPLC results are shown in Figure 6. The peaks of the compound represented by the formula (2) were at 13.5 minutes, 14.2 minutes, and 15.3 minutes, and the peaks of the compound represented by the formula (3) were at 10.5 minutes, 11.3 minutes, and 11.6 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6 minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.009.

[0067] [Synthesis Example 7]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a heating device, and after stirring and dissolving, the mixture was heated to 110°C, and 53 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water distilled out was removed from the system. After reaching 145°C, the mixture was reacted for 4 hours. Then, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize the mixture. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 109 parts by weight of the phenolic resin represented by the formula (4). The hydroxy equivalent of the obtained phenolic resin was 142 g/eq. 78 parts by weight of the obtained phenolic resin represented by

the formula (4) were charged into a reaction vessel with 254 parts by weight of ECH, 64 parts by weight of DMSO, and 13 parts by weight of water, and heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide were charged in portions over 2 hours while maintaining the temperature at 45°C. Then, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60 minutes. Then, after repeated washing with water to remove by-product salts and dimethyl sulfoxide, excess epichlorohydrin was distilled off from the oil layer under reduced pressure with heating to obtain a mixture B containing an epoxy resin, a trace amount of residual solvent, and a trace amount of by-product salts. The theoretical yield of the epoxy resin in this reaction is 109 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B. The methyl isobutyl ketone solution was heated to 70°C, and 7 parts by weight of water, 44 parts by weight of methanol, and 7 parts by weight of 30% aqueous sodium hydroxide solution were added and reacted for 1 hour. The reaction solution was then repeatedly washed with water until the washing solution became neutral. Then, 103 parts by weight of the epoxy resin represented by the formula (1) was obtained by distilling off the methyl isobutyl ketone from the oil layer under reduced pressure with heating (n in formula (1) is 2.3). The epoxy equivalent of the obtained epoxy resin was 266 g/eq.

The HPLC results are shown in Figure 7. The peaks of the compound represented by the formula (2) were at 13.5 minutes, 14.2 minutes, and 15.3 minutes, and the peaks of the compound represented by the formula (3) were at 10.5 minutes, 11.3 minutes, and 11.6 minutes. The ratio b/a of the sum b of the peak areas at 10.5 minutes, 11.3 minutes, and 11.6 minutes to the sum a of the peak areas at 13.5 minutes, 14.2 minutes, and 15.3 minutes was 0.267.

[0068] [Synthesis Example 8]

254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of

sodium hydroxide were charged into a flask equipped with a stirrer, a reflux condenser, and a heating device, and after stirring and dissolving, the mixture was heated to 110°C, and 33 parts by weight of furfural was dropped over 2 hours. After that, the mixture was reacted at 110°C for 3 hours, and then heated to 145°C. During the temperature increase, the water
5 distilled out was removed from the system. Immediately after reaching 145°C, the mixture was cooled to 80°C, and 63 parts by weight of water was charged, and 4 parts by weight of phosphoric acid and 63 parts by weight of 35% hydrochloric acid were added to neutralize. After repeated washing with water, unreacted phenol was distilled off under reduced pressure with heating to obtain 90 parts by weight of the phenolic resin represented by the formula (4).
10 The hydroxy equivalent of the obtained phenolic resin was 141 g/eq. 78 parts by weight of the obtained phenolic resin represented by the formula (4) were charged into a reaction vessel with 254 parts by weight of ECH, 64 parts by weight of DMSO, and 13 parts by weight of water, and the mixture was heated and stirred. After dissolving the phenolic resin and ECH, 23 parts by weight of flaky sodium hydroxide was charged in portions over 2 hours while
15 maintaining the temperature of the solution at 45°C. Thereafter, the reaction was further carried out at 45°C for 2 hours and at 70°C for 60 minutes. Then, excess epichlorohydrin and DMSO were distilled off under reduced pressure with heating to obtain a mixture B containing an epoxy resin represented by the formula (1), a by-product salt, and a trace amount of residual solvent. The theoretical yield of the epoxy resin in this reaction is 109
20 parts by weight.

218 parts by weight of methyl isobutyl ketone was added to dissolve the obtained mixture B, and the by-product salt was removed by washing with water. This methyl isobutyl ketone solution was heated to 70°C, and 22 parts by weight of water, 22 parts by weight of methanol, and 7 parts by weight of 30% aqueous sodium hydroxide solution were added and
25 reacted for 1 hour, after which the reaction solution was repeatedly washed with water until the washings became neutral. Then, methyl isobutyl ketone was distilled off from the oil layer

under reduced pressure with heating to obtain 107 parts by weight of the epoxy resin represented by the above formula (1) (n in formula (1) is 1.7). The epoxy equivalent of the obtained epoxy resin was 204 g/eq.

[0069] [Examples 1 to 4, Comparative Examples 1 to 3]

- 5 The epoxy resins obtained in Synthesis Examples 1 to 7 were used as the base resin, and 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane (abbreviation: TEDDM, manufactured by Tokyo Chemical Industry Co., Ltd., active hydrogen equivalent 78 g/eq.) was used as the curing agent. These were mixed in the weight ratios shown in the formulations in Table 1, and cured at 160°C for 6 hours to produce cured products.

- 10 [0070] The physical properties were measured under the following conditions:

<Conditions for measuring glass transition temperature (T_g)>

Thermomechanical measurement apparatus (TMA): TMA Q400EM manufactured by TA-instruments

Heating rate: 2°C/min

- 15 Measurement temperature range: 25°C to 300°C.

T_g: The point at which the thermal expansion coefficient changes was taken as T_g.

[0071] [Table 1]

		Epoxy Equivalent (g/eq.)	b/a	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Base Resin	Epoxy Resin of Synthesis Example 1	204	0.015	72.3						
	Epoxy Resin of Synthesis Example 2	214	0.015		73.2					
	Epoxy Resin of Synthesis Example 3	218	0.017			73.6				
	Epoxy Resin of Synthesis Example 4	213	0.026				73.2			
	Epoxy Resin of Synthesis Example 5	207	0.009					72.6		
	Epoxy Resin of Synthesis Example 6	211	0.009						73	
	Epoxy Resin of Synthesis Example 7	266	0.267							77.3
Curing Agent	TEDDM			27.6	26.8	26.3	26.8	27.4	27	22.6
Physical Property of Cured Product	Glass Transition Temperature [°C]			170	174	192	184	161	165	145

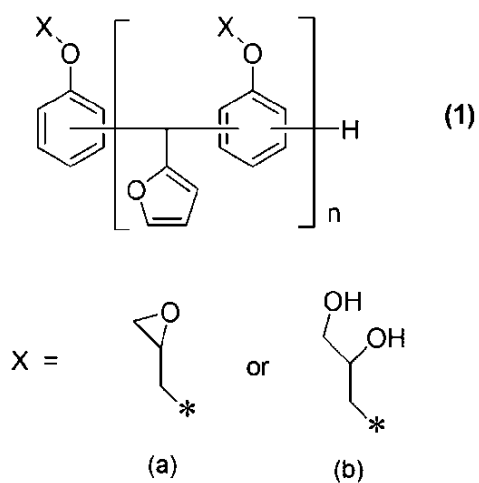
[0072] From the results in Table 1, it was confirmed that the cured products of Examples 1 to 4 of the present invention had higher glass transition points and better heat resistance than the cured products of Comparative Examples 1 to 3.

5 [0073] This application claims priority based on Japanese Patent Application No. 2023-113999, filed on July 11, 2023.

CLAIMS

[Claim 1] An epoxy resin represented by the following formula (1), wherein b/a is 0.012 or more and 0.050 or less, in which “a” is a peak area of a compound represented by the following formula (2) in a chromatogram of high performance liquid chromatography of the epoxy resin, and “b” is a peak area of a compound represented by the following formula (3) in the chromatogram,

[Chem. 1]



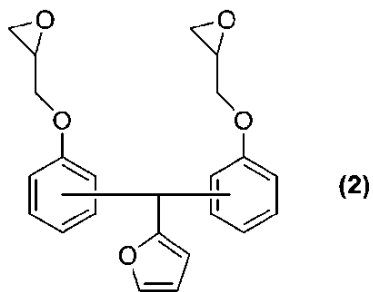
in formula (1), n is an average number of repetitions and is a real number satisfying

10 $1 < n < 15$,

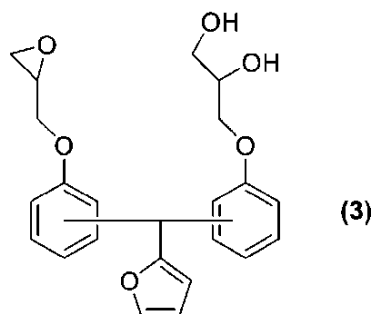
each X is independently a monovalent group represented by formula (a) or formula (b), and at least one X is a monovalent group represented by formula (a), and

* binds to an oxygen atom,

[Chem. 2]



[Chem. 3]



[Claim 2] The epoxy resin according to claim 1, having an epoxy equivalent of 200

5 g/eq. or more and 220 g/eq. or less.

[Claim 3] A curable resin composition comprising the epoxy resin according to claim 1 and a curing agent.

[Claim 4] The curable resin composition according to claim 3, wherein the curing agent is an amine-based curing agent.

10 [Claim 5] A cured product obtained by curing the curable resin composition according to claim 3 or 4.

[Claim 6] A carbon fiber-reinforced composite material obtained by curing the curable resin composition according to claim 3 or 4.