

DESCRIPTION

TITLE OF INVENTION: CURABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF

5 Technical Field

[0001] The present invention relates to a curable resin composition including a specific epoxy resin and a lignin-modified phenolic resin or cashew-modified phenolic resin, and a cured product thereof, and is suitably used in the fields of electrical and electronic components such as semiconductor device encapsulants, printed wiring boards, and buildup laminates, lightweight
10 high-strength materials such as carbon fiber reinforced plastic and glass fiber reinforced plastic, 3D printing applications, and adhesives.

Background Art

[0002] Epoxy resin is widely used in the fields of electrical and electronic components, structural materials, adhesives, paints, etc. for workability and excellent electrical properties, heat resistance,
15 adhesiveness, moisture resistance (water resistance), etc. of the cured product thereof. In recent years, there has been a demand for further improvement of various resin properties such as heat resistance, low dielectric constant, and low dielectric loss tangent along with the development, particularly in the electrical and electronic fields. Furthermore, lightweight materials with excellent mechanical properties are required as the structural materials for applications such as
20 aerospace materials and leisure and sports equipment.

[0003] In recent years, biomass resources have also been attracting attention as carbon-neutral resources from the viewpoint of environmental issues. Furfural is known as a biomass-derived compound, and Patent Document 1 discloses an epoxy resin using furfural as a raw material.

Related Art Document

25 Patent Document

[0004] Patent Document 1: Japanese Patent Application Laid-Open No. 2007-211254

SUMMARY OF INVENTION

Problem to be Solved by the Invention

[0005] However, since Patent Document 1 mixes an epoxy resin using furfural as a raw material with a phenol novolac resin, which is a petrochemical-derived curing agent, to form an epoxy resin composition, the biomass content of the composition is low.

[0006] Generally, an attempt to increase the biomass content makes it difficult to maintain the performance required for a curable resin composition, and therefore, there has been a demand for a curable resin composition that has high biomass content while satisfying the required properties.

[0007] The present invention has been made in view of the above situation, and aims to provide a curable resin composition that has high biomass content and has excellent high heat resistance, low dielectric properties, and mechanical properties, and a cured product thereof.

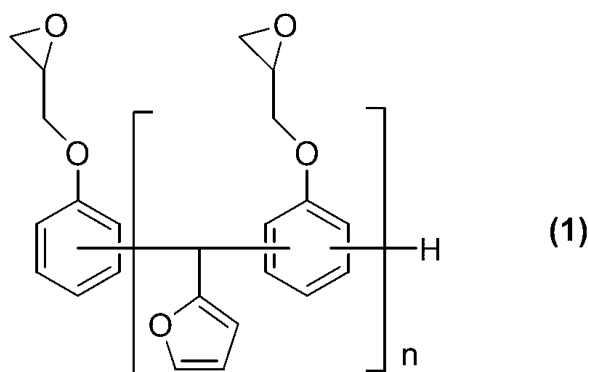
Means for Solving the Problem

[0008] That is, the present invention relates to the following [1] to [9]. It is noted that in the present invention, "(numerical value 1) to (numerical value 2)" indicates that the upper and lower limit values are included.

[1]

A curable resin composition, including an epoxy resin represented by the following formula (1) and a lignin-modified phenolic resin or cashew-modified phenolic resin.

[0009] [Chemical Formula 1]



[0010] (In formula (1), n is an average value of the number of repetitions and represents a real number satisfying $1 < n < 15$.)

[2]

5 The curable resin composition according to [1] above, wherein the lignin-modified phenolic resin or cashew-modified phenolic resin has a biomass content of 20% or more.

[3]

 The curable resin composition according to [1] or [2] above, wherein the epoxy resin has an ICI viscosity (150°C) of 0.01 Pa·s to 0.20 Pa·s.

10 [4]

 The curable resin composition according to any one of [1] to [3] above, having a biomass content of 20% or more.

[5]

 The curable resin composition according to any one of [1] to [4] above, which is for carbon
15 fiber reinforced plastic.

[6]

 The curable resin composition according to any one of [1] to [4] above, which is for semiconductor device encapsulant.

[7]

20 The curable resin composition according to any one of [1] to [4] above, which is for printed wiring board.

[8]

 A cured product, obtained by curing the curable resin composition according to any one of [1] to [7] above.

25 Effects of the Invention

[0011] The present invention relates to a curable resin composition that has high biomass content

and has excellent high heat resistance, low dielectric properties, and mechanical properties. Therefore, the present invention is useful as insulating materials for electrical and electronic components (such as high-reliability semiconductor encapsulant materials), laminates (such as printed wiring boards and buildup substrates), various composite materials including CFRP, adhesives, and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

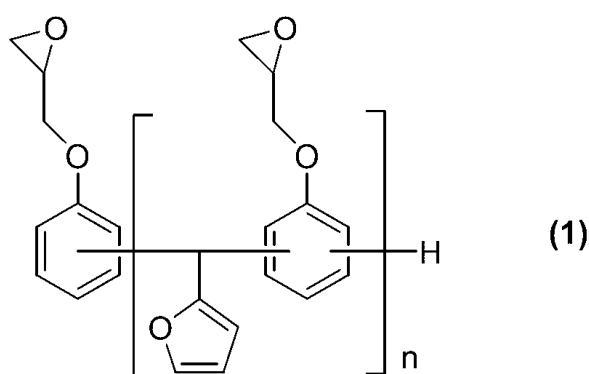
[FIG. 1] shows the GPC chart of Synthesis Example 1.

[FIG. 2] shows the GPC chart of the lignin-modified phenolic resin used in Example 1.

DESCRIPTION OF THE EMBODIMENTS

[0013] The curable resin composition of this embodiment includes an epoxy resin represented by the following formula (1) and a lignin-modified phenolic resin or cashew-modified phenolic resin.

[0014] [Chemical Formula 2]



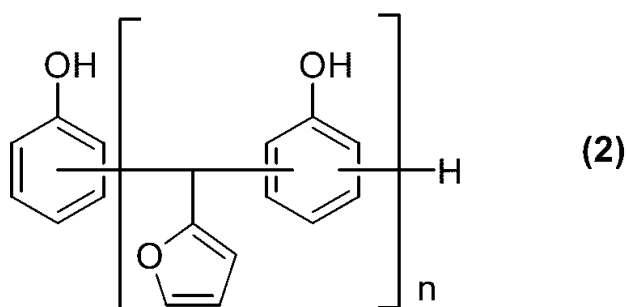
[0015] (In formula (1), n is an average value of the number of repetitions and represents a real number satisfying $1 < n < 15$.)

[0016] In formula (1), the value of n can be calculated from the number average molecular

weight determined by gel permeation chromatography (GPC, detector: RI) measurement of the epoxy resin, or from the area ratio of each separated peak. n is preferably a real number satisfying $1 < n < 15$, more preferably $1 < n < 10$, and particularly preferably $1 < n < 5$.

[0017] The epoxy resin represented by formula (1) can be obtained by reacting a phenolic resin represented by the following formula (2) with epihalohydrin.

[0018] [Chemical Formula 3]



[0019] (In formula (2), n is an average value of the number of repetitions and represents a real number satisfying $1 < n < 15$.)

[0020] The preferred range of n in formula (2) is the same as the range in formula (1).

[0021] The epihalohydrin can be easily obtained from the market. The usage amount of epihalohydrin is preferably 2.0 mol to 10 mol, more preferably 3.0 mol to 8.0 mol, and even more preferably 3.5 mol to 6.0 mol, per 1 mol of hydroxyl groups in the raw material phenol mixture.

[0022] In the above reaction, an alkali metal hydroxide can be used as a catalyst to promote the epoxidation step. Examples of alkali metal hydroxides that can be used include sodium hydroxide, potassium hydroxide, etc., and solid materials may be utilized or aqueous solutions thereof may be used. However, in this embodiment, it is particularly preferable to use solid materials molded into flakes from the viewpoint of solubility and handling.

The usage amount of the alkali metal hydroxide is preferably 0.90 mol to 1.5 mol, more preferably 0.95 mol to 1.25 mol, and even more preferably 0.99 mol to 1.15 mol, per 1 mol of hydroxyl groups in the raw material phenol mixture.

[0023] Further, quaternary ammonium salts such as tetramethylammonium chloride, tetramethylammonium bromide, and trimethylbenzylammonium chloride may be added as a catalyst to promote the reaction. The usage amount of the quaternary ammonium salt is preferably 0.1 g to 15 g, and more preferably 0.2 g to 10 g, per 1 mol of hydroxyl groups in the raw material phenol mixture.

[0024] The reaction temperature is preferably 30°C to 90°C, and more preferably 35°C to 80°C.

Particularly, in this embodiment, the reaction temperature is preferably 50°C or higher, and particularly preferably 60°C or higher, for high-purity epoxidation. The reaction time is preferably 0.5 hours to 10 hours, more preferably 1 hour to 8 hours, and particularly preferably 1 hour to 3 hours. A short reaction time is undesirable because the reaction does not proceed completely, and a long reaction time is undesirable because by-products are formed.

The reaction products of these epoxidation reactions are washed with water, or epihalohydrin, solvent, etc. are removed under heating and reduced pressure without water washing. Furthermore, to obtain an epoxy resin with less hydrolyzable halogen, the recovered epoxy resin can be dissolved using a ketone compound having 4 to 7 carbon atoms (for example, methyl isobutyl ketone, methyl ethyl ketone, cyclopentanone, cyclohexanone, etc.) as a solvent, and an aqueous solution of an alkali metal hydroxide such as sodium hydroxide and potassium hydroxide can be added to conduct a reaction to ensure ring closure. In this case, the usage amount of the alkali metal hydroxide is preferably 0.01 mol to 0.3 mol, and more preferably 0.05 mol to 0.2 mol, per 1 mol of hydroxyl groups in the raw material phenol mixture used for epoxidation. The reaction temperature is preferably 50°C to 120°C, and the reaction time is preferably 0.5 hours to 2 hours.

[0025] After completion of the reaction, the generated salt is removed by filtration, water

washing, or the like, and the solvent is further distilled off under heating and reduced pressure to obtain the epoxy resin represented by the above formula (1).

[0026] As a synthesis method for the phenolic resin represented by the above formula (2), in the case of conducting a reaction (condensation) between furfural and phenols, the amount of phenols is preferably in the range of 1.5 mol to 20 mol, and particularly preferably 3 mol to 10 mol, per 1 mol of furfural.

[0027] Examples of phenols include catechol, resorcinol, and hydroquinone as disubstituted phenols, and phenol as a monosubstituted phenol, and these may be used alone or in combination of two or more types.

[0028] Examples of solvents include methanol, ethanol, propanol, isopropanol, toluene, xylene, etc., but are not limited thereto, and these may be used alone or in combination of two or more types. In the case of using a solvent, the usage amount is preferably in the range of 5 parts by weight to 500 parts by weight, and more preferably 10 parts by weight to 300 parts by weight, per 100 parts by weight of phenol.

[0029] In the above condensation reaction, it is preferable to use a basic catalyst. Although polycondensation is possible with an acidic catalyst, reaction also occurs among furfural, resulting in increased by-products. There is also a method using organometallic compounds, but such a method 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 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 are not limited thereto, and these may be used alone or in combination of two or more types. The usage amount of the catalyst is preferably 0.005 to 2.0 times the molar amount, and more preferably 0.01 to 1.1 times the molar amount, per 1 mol of phenol.

[0030] The condensation reaction in the presence of these basic catalysts is preferably conducted in the range of 40°C to 180°C, and particularly preferably in the range of 80°C to 165°C, and the reaction time is preferably selected in the range of 0.5 hours to 10 hours. The reaction product thus obtained is neutralized so that the system becomes neutral or repeatedly washed with water in the presence of a solvent, and after separating and draining the water, the solvent and unreacted materials are removed under heating and reduced pressure to obtain the phenolic resin represented by the above formula (2).

[0031] The curable resin composition of this embodiment contains a lignin-modified phenolic resin or cashew-modified phenolic resin together with the epoxy resin represented by the above formula (1). The lignin-modified phenolic resin refers to a phenolic resin modified using lignin, and the lignin-modified phenolic resin described in Japanese Patent Application Laid-Open No. 2021-138806 is known. Additionally, PLN-0051LP, which is a lignin-modified phenolic resin, is available from Aica Kogyo Co., Ltd. The cashew-modified phenolic resin refers to a phenolic resin modified using cashew oil, and the cashew-modified phenolic resin described in Japanese Patent Application Laid-Open No. 2007-2032 is known. The lignin-modified phenolic resin or cashew-modified phenolic resin is preferably 0.7 equivalents to 1.2 equivalents per 1 equivalent of epoxy groups of the epoxy resin represented by the above formula (1). In the case of less than 0.7 equivalents or exceeding 1.2 equivalents per 1 equivalent of epoxy groups, curing becomes incomplete in either case, and there is a risk that good cured properties cannot be obtained.

[0032] From the viewpoint of environmental issues, the biomass content of the epoxy resin represented by the above formula (1) is preferably 20% or more. The biomass content of the lignin-modified phenolic resin or cashew-modified phenolic resin is preferably 20% or more. The biomass content of the curable resin composition of this embodiment is preferably 20% or more, and more preferably 25% or more. The upper limit of the biomass content is not particularly limited and may be 100%, but for the balance with cured properties, the upper limit is preferably 60%, and more preferably 40%. A high biomass content can also reduce the usage

amount of fossil resource-based materials represented by petroleum or the like, which is significant from the viewpoint of sustainable use of resources.

[0033] The biomass content of each material and the curable resin composition can be determined by accelerator gravimetric analysis in accordance with ASTM D6866-21.

5 **[0034]** In the curable resin composition of this embodiment, the epoxy resin represented by the above formula (1) can be used alone or in combination with other epoxy resins. In the case of the epoxy resin being used in combination with other epoxy resins, the proportion of the epoxy resin represented by the above formula (1) in the total epoxy resins is preferably 5% by weight to 95% by weight, more preferably 10% by weight to 95% by weight, and even more preferably 15%
10 by weight to 95% by weight. In the case of a small addition amount, sufficient heat resistance may not be exhibited.

[0035] Specific examples of epoxy resins that can be used in combination with the epoxy resin represented by the above formula (1) include polycondensates of bisphenols (bisphenol A, bisphenol F, bisphenol S, biphenol, bisphenol AD, etc.) or phenols (phenol, alkyl-substituted
15 phenol, aromatic-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted dihydroxybenzene, dihydroxynaphthalene, etc.) with various aldehydes (formaldehyde, acetaldehyde, alkyl aldehyde, benzaldehyde, alkyl-substituted benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde, crotonaldehyde, cinnamaldehyde, etc.); polymers of the above phenols with various diene compounds
20 (dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, etc.); polycondensates of the above phenols with ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, etc.); polycondensates of the above phenols with aromatic dimethanols (benzenedimethanol, biphenyldimethanol, etc.); polycondensates of the
25 above phenols with aromatic dichloromethyls (α,α' -dichloroxylene, bischloromethylbiphenyl, etc.); polycondensates of the above phenols with aromatic bisalkoxymethyls

(bismethoxymethylbenzene, bismethoxymethylbiphenyl, bisphenoxymethylbiphenyl, etc.); glycidyl ether epoxy resins obtained by glycidylating polycondensates of the above bisphenols with various aldehydes or alcohols, alicyclic epoxy resins, glycidylamine epoxy resins, glycidyl ester epoxy resins, etc. Specific examples of epoxy resins including plant-derived components include compounds obtained by epoxidizing polycondensates prepared by polycondensing cardanol derived from cashew oil as the above phenols with various aldehydes, and compounds obtained by epoxidizing linseed oil or soybean oil. The epoxy resins are not limited to these as long as the epoxy resins are commonly used. These may be used alone or two or more types may be used. It is particularly preferable to combine with epoxy resins including plant-derived components for the biomass content is increased.

[0036] The curable resin composition of this embodiment may use in combination a curing agent other than the lignin-modified phenolic resin or cashew-modified phenolic resin. Examples include acid anhydride compounds, amine compounds, amide compounds, phenolic compounds, active ester compounds, etc. Specific examples of curing agents that can be used in combination include acid anhydride compounds such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methyladadic anhydride, hexahydrophthalic anhydride, and methylhexahydrophthalic anhydride; amide compounds such as dicyandiamide and polyamide resins synthesized from dimers of linolenic acid and ethylenediamine; aromatic amine compounds such as o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, 2,2'-diaminodiphenylsulfone, diethyltoluenediamine, dimethylthiotoluenediamine, diaminodiphenylmethane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 3,3'-diethyl-4,4'-diaminodiphenylmethane, 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetramethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetraisopropyldiphenylmethane, 4,4'-methylenebis(N-methylaniline), bis(aminophenyl)fluorene,

3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, bis[4-(4-aminophenoxy)phenyl]sulfone, 1,3'-bis(4-aminophenoxy)benzene, 1,4'-bis(4-aminophenoxy)benzene, 1,4'-bis(4-aminophenoxy)biphenyl, 4,4'-(1,3-phenylenediisopropylidene)bisaniiline, 4,4'-(1,4-phenylenediisopropylidene)bisaniiline, naphthalenediamine, benzidine, and dimethylbenzidine; aliphatic amine compounds such as 1,3-bis(aminomethyl)cyclohexane, isophoronediamine, 4,4'-methylenebis(cyclohexylamine), norbornanediamine, ethylenediamine, propanediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, dimerdiamine, and triethylenetetramine; polycondensates of bisphenols (bisphenol A, bisphenol F, bisphenol S, biphenol, bisphenol AD, etc.) or phenols (phenol, alkyl-substituted phenol, aromatic-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted dihydroxybenzene, dihydroxynaphthalene, etc.) with various aldehydes (formaldehyde, acetaldehyde, alkyl aldehyde, benzaldehyde, alkyl-substituted benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde, crotonaldehyde, cinnamaldehyde, etc.), or polymers of the above phenols with various diene compounds (dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, etc.), or polycondensates of the above phenols with ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, etc.), or polycondensates of the above phenols with aromatic dimethanols (benzenedimethanol, biphenyldimethanol, etc.), or polycondensates of the above phenols with aromatic dichloromethyls (α,α' -dichloroxylene, bischloromethylbiphenyl, etc.), or polycondensates of the above phenols with aromatic bisalkoxymethyls (bismethoxymethylbenzene, bismethoxymethylbiphenyl, bisphenoxymethylbiphenyl, etc.), or polycondensates of the above bisphenols with various aldehydes, and modified products thereof; and active ester compounds such as phenol esters, thiophenol esters, N-hydroxyamine esters, and esters of heterocyclic hydroxy compounds, but are not limited thereto.

[0037] The curable resin composition of this embodiment may use a curing accelerator in combination without any problem. Examples of curing accelerators that can be used include imidazoles such as 2-methylimidazole, 2-ethylimidazole, 2-phenylimidazole, and 2-ethyl-4-methylimidazole; tertiary amines such as 2-(dimethylaminomethyl)phenol, triethylenediamine, triethanolamine, and 1,8-diazabicyclo[5,4,0]undecene-7; organic phosphines such as triphenylphosphine, diphenylphosphine, and tributylphosphine; metal compounds such as tin octylate; tetra-substituted phosphonium·tetra-substituted borates such as tetraphenylphosphonium·tetraphenylborate and tetraphenylphosphonium·ethyltriphenylborate; tetraphenylboron salts such as 2-ethyl-4-methylimidazole·tetraphenylborate and N-methylmorpholine·tetraphenylborate; and carboxylic acid compounds such as benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, naphthoic acid, and salicylic acid. The curing accelerator is used as needed in an amount of 0.01 parts by weight to 15 parts by weight relative to 100 parts by weight of epoxy resin.

[0038] The curable resin composition of this embodiment can have an inorganic filler added as needed. Examples of inorganic fillers include powders such as crystalline silica, fused silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, forsterite, steatite, spinel, titania, and talc, or beads obtained by spheroidizing these, but are not limited thereto. These may be used alone or two or more types may be used. The usage amount of these inorganic fillers varies depending on the applications, but for example, in the case of use for semiconductor device encapsulant applications, from the viewpoint of heat resistance, moisture resistance, mechanical properties, flame retardancy, etc. of the cured product of the curable resin composition, the inorganic filler is preferably used in a proportion occupying 20% by weight or more in the curable resin composition, more preferably 30% by weight or more, and particularly preferably used in a proportion occupying 70% by weight to 95% by weight, to improve the coefficient of linear expansion with the lead frame.

[0039] The curable resin composition of this embodiment can be blended with a release agent

to improve mold release during molding. Any known release agent can be used, and examples include ester-based waxes such as carnauba wax and montan wax, fatty acids such as stearic acid and palmitic acid, and metal salts thereof, polyolefin-based waxes such as oxidized polyethylene and non-oxidized polyethylene, etc. These may be used alone or two or more types may be used in combination. The blending amount of these release agents is preferably 0.5% by weight to 3% by weight relative to the total organic components. If the amount is too small, mold release deteriorates, and if too much, adhesion with the lead frame or the like deteriorates.

[0040] The curable resin composition of this embodiment can be blended with a coupling agent to enhance adhesion between the inorganic filler and resin components. Any known coupling agent can be used, and examples include various alkoxysilane compounds such as vinylalkoxysilane, epoxyalkoxysilane, styrylalkoxysilane, methacryloxyalkoxysilane, acryloxyalkoxysilane, aminoalkoxysilane, mercaptoalkoxysilane, and isocyanate alkoxysilane, alkoxytitanium compounds, aluminum chelates, etc. These may be used alone or two or more types may be used in combination. As for the method of adding the coupling agent, the surface of the inorganic filler may be treated with the coupling agent in advance and then kneaded with the resin, or the coupling agent may be mixed with the resin and then the inorganic filler may be kneaded.

[0041] The curable resin composition of this embodiment can be blended with known additives as needed. Specific examples of additives that can be used include polybutadiene and modified products thereof, modified products of acrylonitrile copolymers, polyphenylene ether, polystyrene, polyethylene, polyimide, fluorine resins, maleimide-based compounds, cyanate ester-based compounds, silicone gel, silicone oil, colorants such as carbon black, phthalocyanine blue, and phthalocyanine green, etc.

[0042] The curable resin composition of this embodiment is obtained by uniformly mixing the above components. The production method of the curable resin composition of this embodiment is not particularly limited, and for example, the curable resin composition can be obtained by

sufficiently mixing the epoxy resin with a curing agent, a curing accelerator, an inorganic filler, a release agent, a silane coupling agent, additives, etc. using an extruder, kneader, roll, planetary mixer, or the like until uniformity is achieved.

[0043] The obtained curable resin composition can take various forms such as a resin sheet, a prepreg, or the like depending on the molding method. The prepreg form can be obtained, for example, by heating and melting the curable resin composition and/or a resin sheet of this embodiment to reduce viscosity and impregnating the composition into a fiber substrate.

[0044] The curable resin composition of this embodiment can be dissolved in solvents such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide, and N-methylpyrrolidone as needed to form a varnish-like composition (hereinafter also simply referred to as varnish), and a prepreg can be manufactured by impregnating the composition into a substrate such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, alumina fibers, and paper, followed by heating and drying. The solvent used in this case occupies an amount of 10% by weight to 70% by weight, and preferably 15% by weight to 70% by weight, in the mixture of the curable resin composition of this embodiment and the solvent.

[0045] Carbon fiber reinforced plastic (CFRP) can be obtained by cutting and laminating the above prepreg into a desired shape, and then heating and curing the epoxy resin composition while applying pressure to the laminate by press molding, autoclave molding, sheet winding molding, or other methods. Additionally, copper foil or an organic film can also be laminated during prepreg lamination.

[0046] CFRP can also be molded using known methods in addition to the above methods. For example, resin transfer molding technology (RTM method) can be used, in which a carbon fiber substrate (usually, carbon fiber fabric is used) is cut, laminated, and shaped to manufacture a preform (preformed body before resin impregnation), the preform is placed in a molding die and the die is closed, resin is injected to impregnate and cure the preform, and then the die is opened

to remove the molded product. Additionally, as a type of RTM method, for example, VaRTM (Vacuum assist Resin Transfer Molding) method, SCRIMP (Seeman's Composite Resin Infusion Molding Process) method, CAPRI (Controlled Atmospheric Pressure Resin Infusion) method described in Japanese Patent Publication No. 2005-527410 that evacuates a resin supply tank to a pressure lower than atmospheric pressure, uses circulation compression, and controls net molding pressure to more appropriately control the resin injection process, particularly the VaRTM method, can also be used. Furthermore, a film stacking method in which a fiber substrate is sandwiched between resin sheets (films), a method of adhering powdered resin to a reinforcing fiber substrate for improved impregnation, a molding method using a fluidized bed or fluid slurry method in the process of mixing resin with a fiber substrate (Powder Impregnated Yarn), and a method of blending resin fibers with a fiber substrate can also be used.

[0047] Examples of carbon fibers include acrylic-based, pitch-based, and rayon-based carbon fibers, among which acrylic-based carbon fibers with high tensile strength are preferably used. As forms of carbon fibers, twisted yarn, untwisted yarn, and non-twisted yarn can be used, but untwisted yarn or non-twisted yarn is preferably used because such yarn provides a good balance between moldability and strength characteristics of fiber reinforced composite materials.

[0048] The cured product of the curable resin composition of this embodiment can be used for various applications other than the above-mentioned CFRP applications, for example, adhesives, paints, coating agents, molding materials (including sheets, films, CFRP, rotor fixing members, etc.), semiconductor device encapsulant, liquid crystal display device encapsulant, organic EL device encapsulant, electrical and electronic components such as printed wiring boards (BGA substrates, buildup substrates, etc.), 3D printing, and additives for other resins.

[0049] Examples of adhesives include adhesives for civil engineering, construction, automotive, general office, and medical use, as well as adhesives for electronic materials. Among these, examples of adhesives for electronic materials include interlayer adhesives for multilayer substrates such as buildup substrates, die bonding agents, semiconductor adhesives such as

underfill, BGA reinforcement underfill, mounting adhesives such as anisotropic conductive film (ACF) and anisotropic conductive paste (ACP), etc., which are suitable for various applications.

[0050] In the case of applying the curable resin composition of this embodiment to semiconductor device encapsulant, a cured product can be obtained by placing the curable resin composition of this embodiment and a lead frame or semiconductor package substrate equipped with semiconductor devices in a mold, molding by a melt casting method or transfer molding method, injection molding method, compression molding method, or the like, and further heating at 80°C to 200°C for 2 hours to 10 hours. Examples of semiconductor devices manufactured using this encapsulant include potting, dipping, and transfer mold encapsulation for capacitors, transistors, diodes, light emitting diodes, IC, LSI, etc., potting encapsulation for COB, COF, TAB, etc. of IC and LSI, underfill for flip chips, encapsulation during mounting of IC packages such as QFP, BGA, and CSP (including reinforcement underfill), etc.

[0051] In the case of applying the curable resin composition of this embodiment to printed wiring board, a prepreg can also be obtained by heating and melting the curable resin composition to reduce viscosity and impregnating into reinforcing fibers such as glass fibers and polyamide fibers. Specific examples include glass fibers such as E-glass cloth, D-glass cloth, S-glass cloth, Q-glass cloth, spherical glass cloth, NE-glass cloth, and T-glass cloth, and/or organic fibers, but are not particularly limited thereto. The shape of the substrate is not particularly limited, but examples include woven fabric, non-woven fabric, roving, chopped strand mat, etc. As for the weaving method of woven fabric, plain weave, mock leno weave, twill weave, etc. are known, and these known methods can be appropriately selected and used according to the intended applications and performance. Further, glass woven fabric that has been subjected to fiber opening treatment or surface treatment with silane coupling agent or the like is preferably used. The thickness of the substrate is not particularly limited, but is preferably about 0.01 mm to 0.4 mm. Further, a prepreg can also be obtained by impregnating reinforcing fibers with the varnish and heating and drying, and a copper clad laminate (CCL) can be manufactured based on this.

By hot press molding the obtained prepreg and CCL, a laminate using the curable resin composition of this embodiment can also be manufactured. The laminate is not particularly limited as long as the laminate includes one or more prepregs, and may have any other layers. In addition, a sheet-like adhesive can be obtained by applying the varnish on a release film and removing the solvent under heating to achieve B-staging. This sheet-like adhesive can be used as an interlayer insulating layer in multilayer substrates or the like or as an adhesive sheet for mounting semiconductors. Furthermore, the curable resin composition of this embodiment can be suitably used for special substrate materials such as package substrate (substrate) and HDI (high density interconnect).

[0052] In the case of using the curable resin composition of this embodiment for rotor fixing member, a cured product can be obtained by placing the curable resin composition of this embodiment in a mold for rotor fixing member, molding by a melt casting method or transfer molding method, injection molding method, compression molding method, or the like, and further heating at 80°C to 200°C for 2 hours to 10 hours.

Examples

[0053] The present invention will be described more specifically below by citing 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. Accordingly, the scope of the present invention should not be interpreted in a limited manner to the specific examples shown below. Hereinafter, unless otherwise specified, parts refer to parts by weight.

[0054] Various analytical methods were performed under the following conditions.

- Epoxy equivalent

Measured by the method described in JIS K-7236, and the unit is g/eq.

- Softening point

Measured by the method in accordance with JIS K-7234, and the unit is °C.

- Melt viscosity

Measured by ICI melt viscosity (150°C) cone plate method, and the unit is Pa·s.

- Biomass content analysis (accelerator gravimetric analysis)

5 Measured and calculated in accordance with ASTM D6866-21. The unit is %.

[0055] [Synthesis Example 1]

In a flask equipped with a stirrer, a reflux condenser, and a stirring device, 254 parts by weight of phenol, 63 parts by weight of water, and 27 parts by weight of sodium hydroxide were charged, and after stirring and dissolution, the mixture was heated to 110°C, and 44 parts by weight of
10 furfural was added dropwise over 2 hours. After reacting at 110°C for 3 hours, the temperature was raised to 145°C. During the temperature rise, water that distilled out was removed from the system. After reaching 145°C, the reaction was continued 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 for neutralization. After repeated
15 washing with water, unreacted phenol was distilled off under heating and reduced pressure to obtain 109 parts by weight of phenolic resin. To 78 parts by weight of the obtained phenolic resin, 254 parts by weight of epichlorohydrin (ECH, same hereinafter), 64 parts by weight of dimethyl sulfoxide (DMSO, same hereinafter), and 13 parts by weight of water were charged into a reaction vessel, and after heating, stirring, and dissolution, while maintaining the temperature at
20 45°C, 23 parts by weight of flake sodium hydroxide was charged in portions over 2 hours. Thereafter, the reaction was further continued 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 heating and reduced pressure, and 218 parts by weight of methyl isobutyl ketone was added to the residue and dissolved. This methyl
25 isobutyl ketone solution was heated to 70°C, 7 parts by weight of 30% sodium hydroxide aqueous

solution was added, and after reacting for 1 hour, the reaction solution was repeatedly washed with water until the washing solution became neutral. Then, methyl isobutyl ketone was distilled off from the oil layer under heating and reduced pressure to obtain 97 parts by weight of epoxy resin A represented by the above formula (1). The epoxy equivalent was 214 g/eq., the softening point was 49°C, the ICI melt viscosity was 0.04 Pa·s, the average value $\bar{n}$ of the number of repetitions from GPC was 2.1, and the biomass content was 25%. The GPC chart of epoxy resin A is shown in FIG. 1.

[0056] [Synthesis Example 2]

A cashew-modified phenolic resin was synthesized according to Japanese Patent Application Laid-Open No. 2007-2032. In a flask equipped with a stirrer, a reflux condenser, and a stirring device, 250 parts by weight of phenol, 138 parts by weight of 37% formalin, 110 parts by weight of cashew oil, and 2 parts by weight of sulfuric acid were charged, and the reaction was carried out under reflux at 100°C for 1 hour. Subsequently, the temperature was raised to 190°C while performing vacuum distillation to obtain 254 parts by weight of cashew-modified phenolic resin. The softening point of this resin was 80°C, and the biomass content was 31%.

[0057] [Example 1]

Using the epoxy resin A obtained in Synthesis Example 1 as the main agent, a lignin-modified phenolic resin (PLN-0051LP manufactured by Aica Kogyo Co., Ltd., softening point is 106°C, GPC chart is shown in FIG. 2) as a curing agent, and TPP (triphenylphosphine) as a curing accelerator were blended and kneaded at the weight ratio shown in the blending composition of Table 1, and cured under curing conditions of 180°C for 6 hours to prepare a cured product.

[0058] [Example 2]

Using the epoxy resin A obtained in Synthesis Example 1 as the main agent, the cashew-modified phenolic resin obtained in Synthesis Example 2 as a curing agent, and TPP (triphenylphosphine) as a curing accelerator were blended and kneaded at the weight ratio shown

in the blending composition of Table 1, and cured under curing conditions of 180°C for 6 hours to prepare a cured product.

[0059] [Comparative Example 1]

Using the epoxy resin A obtained in Synthesis Example 1 as the main agent, PN (phenol novolac resin, manufactured by Meiwa Kasei Co., Ltd., hydroxyl equivalent 103 g/eq.) as a curing agent, and TPP (triphenylphosphine) as a curing accelerator were blended and kneaded at the weight ratio shown in the blending composition of Table 1, and cured under curing conditions of 180°C for 6 hours to prepare a cured product.

[0060] The physical property values were measured under the following conditions.

<Heat Resistance (T_g) Measurement Conditions>

Dynamic viscoelasticity measuring instrument: TA-instruments, DMA-Q800

Measurement temperature range: 25°C to 300°C

Heating rate: 2°C/min

T_g: The peak point of Tanδ was taken as T_g.

<Dielectric Constant and Dielectric Loss Tangent Test>

Testing was conducted using a 10 GHz cavity resonator manufactured by AET Co., Ltd. at 25°C by the cavity resonator perturbation method. The sample size was 2.5 mm width × 50 mm length, and the test was conducted with a thickness of 0.3 mm.

<Tensile Modulus, Maximum Tensile Stress>

Using an Autograph AGS-X manufactured by Shimadzu Corporation, the test piece was clamped so that the length became 5 cm at a tensile speed of 0.5 mm/min, and tensile measurement was performed by pulling in the 180° direction at the above test speed.

[0061] [Table 1]

	Example 1	Example 2	Comparative Example 1
Epoxy resin A	63	61	68
Lignin-modified phenolic resin	37	-	-
Cashew-modified phenolic resin	-	39	

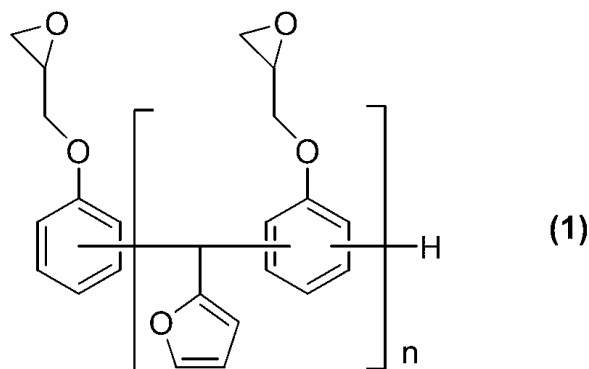
PN	-	-	32
TPP	1	1	1
Evaluation result			
Tg (°C)	154	140	145
Dielectric constant	3.01	2.89	3
Dielectric loss tangent	0.031	0.028	0.033
Tensile modulus (GPa)	2.8	2.3	2.3
Maximum tensile stress (MPa)	40	64	61
Biomass content (%)	26	27	17

[0062] From the results in Table 1, it was confirmed that Examples 1 and 2 had high biomass content and had excellent high heat resistance, low dielectric properties, and mechanical properties.

CLAIMS

[Claim 1] A curable resin composition, comprising an epoxy resin represented by the following formula (1) and a lignin-modified phenolic resin or cashew-modified phenolic resin,

[Chemical Formula 1]



(in formula (1), n is an average value of the number of repetitions and represents a real number satisfying $1 < n < 15$).

[Claim 2] The curable resin composition according to claim 1, wherein the lignin-modified phenolic resin or cashew-modified phenolic resin has a biomass content of 20% or more.

[Claim 3] The curable resin composition according to claim 1, wherein the epoxy resin has an ICI viscosity (150°C) of 0.01 Pa·s to 0.20 Pa·s.

[Claim 4] The curable resin composition according to claim 1, having a biomass content of 20% or more.

[Claim 5] The curable resin composition according to any one of claims 1 to 4, which is for carbon fiber reinforced plastic.

[Claim 6] The curable resin composition according to any one of claims 1 to 4, which is for semiconductor device encapsulant.

[Claim 7] The curable resin composition according to any one of claims 1 to 4, which is for printed wiring board.

[Claim 8] A cured product, obtained by curing the curable resin composition according to any one of claims 1 to 4.