In the reaction, an alkali metal hydroxide can be used as a catalyst that promotes the epoxidation process. Examples of alkali metal hydroxides that can be used include sodium hydroxide and potassium hydroxide, and a solid may be used or an aqueous solution thereof may be used. However, in the present invention, particularly, it is preferable to use a solid molded into flakes in consideration of solubility and handling. The amount of the alkali metal hydroxide used with respect to 1 mol of the hydroxyl group of the raw material phenolic resin is generally 0.90 to 1.50 mol, and particularly preferably 1.01 to 1.35. If the amount is less than 0.90, the amount of compounds for which epoxidation is not completed increases, and the amount of chlorine increases, which tends to cause corrosion. In addition, if the amount is more than 1.5, hydroxide ions react with the epoxy groups formed, an α-glycol structure is more likely to be formed, a decrease in crosslink density is caused, and thus the above range is preferable.

[0037]

In addition, in order to promote the reaction, a quaternary ammonium salt such as tetramethylammonium chloride, tetramethylammonium bromide, or trimethylbenzylammonium chloride may be added as a catalyst. The amount of the quaternary ammonium salt used with respect to 1 mol of the hydroxyl group of the raw material phenolic resin is generally preferably 0.0009 to 0.15 mol.

[0038]

During the epoxidation reaction, in the present invention, sulfur is introduced into the molecule by reacting the sulfur-containing compound at the same time. The sulfur-containing compound is not particularly limited as long as it contains sulfur in its structure, and thioether compounds and disulfide compounds may be exemplified. Specifically, it is possible to obtain an epoxy resin mixture containing a sulfur-containing compound by adding thioether compounds having 1 to 10 carbon atoms such as dimethyl

sulfide, diallyl sulfide, diethyl sulfide, and methylphenyl sulfide, disulfide compounds having 1 to 10 carbon atoms such as dimethyl disulfide, diallyl disulfide, dibutyl disulfide, and diphenyl disulfide, sulfur-containing compounds such as trisulfides having 1 to 10 carbon atoms such as dimethyl trisulfide and dipropyl trisulfide or the like. The sulfur-containing compound preferably has 2 to 4 carbon atoms and dimethyl sulfide and dimethyl disulfide are particularly preferable. This is because the unreacted sulfide compound is easily removed in a subsequent process due to its low molecular weight. The amount of the sulfur compound added with respect to 1,000 parts by weight of the raw material phenolic resin is generally preferably 0.1 to 50 parts by weight, more preferably 0.5 to 40 parts by weight, and particularly preferably 1 to 30 parts by weight. If the amount of the sulfur-containing compound added is less than the above range, the content of the sulfur-containing compound in the epoxy resin mixture after the reaction process is completed becomes small, and it is not possible to obtain excellent mechanical strength and toughness. On the other hand, if the content of the sulfur-containing compound is larger than the above range, the content of the sulfur-containing compound in the epoxy resin mixture after the reaction process is completed becomes too large, which causes corrosion in the metal wiring in a high temperature range as described above. If the amount of the sulfur compound added is within the above range, there is little effect on corrosion in the metal wiring, and it is possible to obtain excellent mechanical strength and toughness.

[0039]

The reaction temperature during epoxidation is generally 30 to 90°C, and preferably 35 to 80°C. The reaction time is generally 0.5 to 10 hours and preferably 1 to 8 hours.

After the reaction is completed, the reaction product is washed with water or epihalohydrin, the solvent and the like are removed by heating under a reduced pressure without washing with water, and the epoxy resin represented by Formula (2) is then obtained. In addition, in order to produce an epoxy resin with less hydrolyzable halogen, the collected epoxy resin is dissolved in a solvent such as toluene or methyl isobutyl ketone, an aqueous solution of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide is added for the reaction, and ring closure can be secured. In this case, the amount of the alkali metal hydroxide used with respect to 1 mol of the hydroxyl group of the phenol compound used for glycidylation is generally 0.01 to 0.3 mol, and preferably 0.05 to 0.2 mol. The reaction temperature is generally 50 to 120℃, and the reaction time is generally 0.5 to 2 hours.

[0040]

After the reaction is completed, the produced salt is removed by filtration, washing with water, or the like, and the solvent is additionally distilled off by heating under a reduced pressure, and thereby an epoxy resin mixture of the present invention is obtained.

[0041]

The epoxy resin composition of the present invention contains a curing agent. Examples of curing agents that can be used include phenol-based curing agents, acid anhydrate-based curing agents, amide-based curing agents, and amine-based curing agents.

[0042]

In the epoxy resin composition of the present invention, particularly, a phenolic resin having a repeating unit is preferable as a phenol-based curing agent because it can achieve both heat resistance and thermal stability of the cured product in a well-balanced

manner. Examples of phenol-based curing agents include, as phenolic resins, phenol novolac resins, cresol novolak resins, and phenol aralkyl resins; 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, resorcinol, naphthalenediol, tris-(4-hydroxyphenyl)methane and 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, etc.); phenolic resins obtained by condensation of phenols (for example, phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene and dihydroxynaphthalene, etc.) and aldehydes (formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde and furfural, etc.), ketones (p-hydroxyacetophenone and o-hydroxyacetophenone, etc.) or dienes (dicyclopentadiene and tricyclopentadiene, etc.); phenolic resins obtained by polycondensation of the 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 and 1,4-bis(hydroxymethyl)benzene, etc.); modified products of the phenols and/or the phenolic resins; and halogenated phenols such as tetrabromobisphenol A and brominated phenolic resins.

[0043]

Examples of acid anhydrate-based curing agents include phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, nadic methyl anhydride, hexahydrophthalic anhydride and methylhexahydrophthalic anhydride.

[0044]

Examples of amide-based curing agents include dicyandiamide and polyamide resins synthesized from a linolenic acid dimer and ethylene diamine.

[0045]

As the amine-based curing agent, 3,3’-diaminodiphenylsulfone (3,3’-DDS), 4,4’-diaminodiphenylsulfone (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, 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-ethylhexanoic acid ester of 2,4,6-tris(dimethylaminomethyl)phenol and the like can be used. In addition, examples thereof include aniline novolak, orthoethyl aniline novolak, aniline resins obtained by reacting aniline with xylylene chloride, and aniline resins obtained by polycondensation of aniline 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 and 1,4-bis(hydroxymethyl)benzene, etc.).

[0046]

In the epoxy resin composition of the present invention, the amount of the curing agent used with respect to 1 equivalent of the epoxy group of the epoxy resin is preferably 0.7 to 1.2 equivalent. If the amount is less than 0.7 equivalent or more than 1.2 equivalent with respect to 1 equivalent of the epoxy group, curing may be incomplete

and favorable cured product properties may not be obtained.

[0047]

In addition, in the epoxy resin composition of the present invention, a curing accelerator may be added as necessary. A gelling time can be adjusted using a curing accelerator. 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, phosphines or phosphonium compounds such as triphenylphosphine, tri(tolyl)phosphine, tetraphenylphosphonium bromide, and tetraphenylphosphoniumtetraphenylborate, metal compounds such as tin octylate, tetra-substituted phosphonium/tetra-substituted borates such as tetraphenyl phosphonium/tetraphenylborate, and tetraphenylphosphonium/ethyltriphenylborate, and tetraphenylboron salts such as 2-ethyl-4-methylimidazole/tetraphenylborate and N-methylmorpholine/tetraphenylborate. 0.01 to 5.0 parts by weight of the curing accelerator with respect to 100 parts by weight of the epoxy resin is used as necessary.

[0048]

In the epoxy resin composition of the present invention, other epoxy resins may be added. Specific examples thereof include polycondensatea of phenols (phenol, alkyl-substituted phenol, aromatic-substitution 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.), polymers of phenols and various diene compounds (dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene,

vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenyl biphenyl, butadiene, isoprene, etc.), polycondensates 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 and 1,4-bis(hydroxymethyl)benzene, etc.), polycondensates of bisphenols and various aldehydes, glycidyl ether-based epoxy resins obtained by glycidylating alcohols and the like, alicyclic epoxy resins represented by 4-vinyl-1-cyclohexene diepoxide or 3,4-epoxycyclohexylmethyl-3,4'-epoxycyclohexanecarboxylate, glycidyl amine-based epoxy resins represented by tetraglycidyl diaminodiphenylmethane (TGDDM) or triglycidyl-p-aminophenol, and glycidyl ester-based epoxy resins, but the present invention is not limited as long as they are epoxy resins that are generally used.

[0049]

In addition, an inorganic filler can be added to the epoxy resin composition of the present invention as necessary. Examples of inorganic fillers include powders of crystalline silica, fused silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, forsterite, steatite, spinel, titania, talc and the like and beads made by spheroidizing these powders, but the present invention is not limited thereto. These may be used alone or two or more thereof may be used. The amount of these inorganic fillers used varies depending on applications, and for example, when fillers are used as the encapsulant for semiconductors, in terms of the heat resistance, moisture resistance, mechanical properties, flame retardance and the like of the cured product of the epoxy resin composition, the proportion of the fillers used in the epoxy resin composition is preferably 20 wt% or more, more preferably 30 wt% or

more, and particularly preferably 70 to 95 wt% in order to increase the linear expansion coefficient with a lead frame.

[0050]

A release agent can be added to the epoxy resin composition of the present invention in order to facilitate release from a mold during molding. As the release agent, any of conventionally known agents can be used, and examples thereof include ester waxes such as carnauba wax and montan wax, fatty acids such as stearic acid and palmitic acid and metal salts thereof, and polyolefin waxes such as oxidized polyethylene and non-oxidized polyethylene. These may be used alone or two or more thereof may be used in combination. The amount of these release agents added with respect to the total organic component is preferably 0.5 to 3 wt%. If the amount is too small, release from the mold becomes poor, and if the amount is too large, adhesion to the lead frame or the like becomes poor.

[0051]

A coupling agent can be added to the epoxy resin composition of the present invention in order to improve adhesion between the inorganic filler and the resin component. As the coupling agent, any of conventionally known agents can be used, and examples thereof include various alkoxysilane compounds such as vinylalkoxysilane, epoxyalkoxysilane, styrylalkoxysilane, methacryloxyalkoxysilane, acryloxyalkoxysilane, aminoalkoxysilane, mercaptoalkoxysilane, and isocyanatoalkoxysilane, alkoxy titanium compounds, and aluminum chelates. These may be used alone or two or more thereof may be used in combination. As the method of adding a coupling agent, the surface of the inorganic filler may be treated with a coupling agent in advance and then kneaded with the resin or the resin may be mixed with the coupling agent and then kneaded with the inorganic filler.

[0052]

In addition, a known additive can be added to the epoxy resin composition of the present invention as necessary. Specific examples of additives that can be used include polybutadiene and their modified products, modified products of acrylonitrile copolymers, polyphenylene ether, polystyrene, polyethylene, polyimide, fluorine resin, maleimide compound, cyanate ester compounds, silicone gel, silicone oil, and coloring agents such as carbon black, phthalocyanine blue, and phthalocyanine green.

[0053]

A known maleimide compound can be added to the epoxy resin composition of the present invention as necessary. Specific examples of maleimide compounds that can 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'-diphenylmethanebismaleimide, 4-methyl-1,3-phenylene bismaleimide, 4,4'-diphenyl ether bismaleimide, 4,4'-diphenylsulfone bismaleimide, 1,3-bis(3-maleimidophenoxy)benzene, and 1,3-bis(4-maleimidophenoxy)benzene, but the present invention is not limited thereto. These may be used alone or two or more thereof may be used in combination. When a maleimide compound is added, a curing accelerator is added as necessary, and the curing accelerator and radical polymerization initiators such as organic peracids and azo compounds can be used.

[0054]

The epoxy resin composition of the present invention is obtained by uniformly mixing the above components. The epoxy resin composition of the present invention can be easily cured into a cured product by the same method as the conventionally known method. For example, an epoxy resin, a curing agent, and as necessary, a curing accelerator, an inorganic filler, a release agent, a silane coupling agent and an additive are

sufficiently mixed using an extruder, a kneader, a roller or the like as necessary, until the mixture becomes uniform, and thereby an epoxy resin composition of the present invention is obtained, this composition is molded using a melt casting method, a transfer molding method, an injection molding method, a compression molding method or the like, and additionally heated at 80 to 200°C for 2 to 10 hours, and thereby a cured product can be obtained.

[0055]

In addition, the epoxy resin composition of the present invention may contain a solvent as necessary. An epoxy resin composition containing a solvent (epoxy resin varnish) can be made into a cured product of the epoxy resin composition of the present invention by hot-press molding a prepreg obtained by impregnating a fibrous material (base material) such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, alumina fibers, and paper and heating and drying it. The content of the solvent in the epoxy resin composition is generally 10 to 70 wt%, and preferably about 15 to 70 wt%. Examples of solvents include amide solvents such as γ-butyrolactones, N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylimidazolidinone; sulfones such as tetramethylene sulfone; ether solvents such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether monoacetate, and propylene glycol monobutyl ether, and preferably mono- or di-lower (C1-3) alkyl ethers of lower (C1-3) alkylene glycol; ketone solvents such as methyl ethyl ketone and methyl isobutyl ketone and preferably, di-lower (C1-3) alkyl ketone in which two alkyl group may be the same as or different from each other; and aromatic solvents such as toluene and xylene. These may be used alone or a mixed solvent of two or more thereof may be used.

[0056]

In addition, a sheet-like adhesive (a sheet of the present invention) can be obtained by applying the epoxy resin varnish onto a release film, removing the solvent under heating, and performing B stage. This sheet-like adhesive can be used as an interlayer insulating layer in a multi-layer substrate or the like.

[0057]

In addition, a prepreg of the present invention can be obtained by heating and melting the epoxy resin composition and/or the resin sheet of the present invention to lower its viscosity, and impregnating it with a fiber base material.

[0058]

In addition, a prepreg of the present invention can also be obtained by impregnating a varnish-like epoxy resin composition with a fiber base material and heating and drying it. After the prepreg is cut into a desired shape and laminated, the epoxy resin composition is heated and cured while applying pressure to the laminate using a press molding method, an autoclave molding method, a sheet winding molding method or the like, and thereby an FRP of the present invention can be obtained. In addition, a copper foil or an organic film can also be laminated when the prepreg is laminated.

[0059]

In addition, regarding an FRP molding method of the present invention, in addition to the above method, an FRP can be obtained by molding according to known methods. For example, a resin transfer molding technique (RTM method) in which a carbon fiber base material (generally, a carbon fiber fabric is used) is cut, laminated, and shaped to produce a preform (a preform component before it is impregnated with a resin), the preform is placed in a mold, the mold is closed, a resin is injected and impregnated into the preform and cured, the mold is the opened, and the molded product is taken out

can also be used.

In addition, a kind of RTM method, for example, a VaRTM method, a Seeman's Composite Resin Infusion Molding Process (SCRIMP) method, a Controlled Atmospheric Pressure Resin Infusion (CAPRI) method in which a resin supply tank described in Published Japanese Translation No. 2005-527410 of the PCT International Publication is evacuated to a pressure lower than atmospheric pressure, and by using circulation compression and controlling a net molding pressure, a resin injection process, particularly, a VaRTM method, is better controlled can also be used.

[0060]

In addition, a film stacking method in which a fiber base material is inserted into a resin sheet (film), a method of adhering a powder resin to a reinforcing fiber base material in order to improve impregnation, a molding method (Powder Impregnated Yarn) using a fluidized bed or a fluid slurry method in a procedure of mixing a resin with a fiber base material, and a method of mixing resin fibers into a fiber base material can also be used.

[0061]

Examples of carbon fibers include acrylic, pitch, and rayon carbon fibers, and among these, acrylic carbon fibers having high tensile strength are preferably used. As the form of carbon fibers, a twisted yarn, an untwisted yarn, a non-twisted yarn and the like can be used, but an untwisted yarn or a non-twisted yarn is preferably used because moldability and strength properties of a fiber- reinforced composite material are well-balanced.

[0062]

The cured product obtained in the present invention can be used for various applications other than the above substrates and CFRP. Specifically, general

applications in which a thermosetting resin such as an epoxy resin is used may be exemplified, and for example, in addition to adhesives, paints, coating agents, mold materials (including sheets, films, FRP, etc.), insulating materials (including wire coatings, etc.), and encapsulants, additives for other resins and the like may be exemplified.

[0063]

Examples of adhesives include adhesives for civil engineering, adhesives for construction, adhesives for automobiles, adhesives for general office, and adhesives for medical care, as well as adhesives for electronic materials. Among these, adhesives for electronic materials include, for example, interlayer adhesives for multi-layer substrates such as build-up substrates, adhesives for semiconductors such as die bonding agents and underfills, and adhesives for mounting such as underfills for BGA reinforcement, anisotropic conductive films (ACF), and anisotropic conductive pastes (ACP).

[0064]

Examples of encapsulants include potting, dipping, and transfer mold encapsulants for capacitors, transistors, diodes, light emitting diodes, ICs, and LSIs, potting encapsulants for COB, COF, TAB and the like of IC, and LSIs, and encapsulants (including underfills for reinforcement) when IC packages such as underfills for flip chips, QFP, BGA, and CSP are mounted.

[Examples]

[0065]

The present invention will be described below in more detail with reference to examples. The materials, treatment details, treatment procedures and the like shown below can be appropriately changed without departing from the spirit and scope of the present invention. Therefore, the scope of the present invention should not be construed

as limited to the following specific examples.

[0066]

Various analysis methods were performed under the following conditions.

·Epoxy equivalent

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

·Softening point

measured by the method according to JIS K-7234, and the unit was ℃.

·Melt viscosity

ICI melt viscosity (150℃) measured by a cone-plate method, and the unit was Pa·s.

[0067]

·GPC (gel permeation chromatography) analysis

Manufacturer: Waters

Device: alliance Waters e2695

Column: guard column SHODEX GPC KF-601 (2 columns), KF-602 KF-602.5, KF-603

Flow rate: 1.23 ml/min.

Column temperature: 25℃

Solvent used: THF (tetrahydrofuran)

Detector: RI (differential refraction detector)

[0068]

·Sulfur content analysis (combustion method)

[Thermal decomposition process]

Device instrument manufacturer: Thermo SCIENTIFIC combustion ion chromatography system

(Thermal decomposition condition)

Combustion temperature of 1,000℃, maintained for 15 minutes

Gas flow rate Ar 200 ml/min O_2 400 ml/min

Sample 0.05g

(Decomposition gas absorption solution)

Phosphate ion standard solution 1,000 ppm 1 mL

H_2O_2 30% 0.05 mL

diluted with water to prepare 500 mL

[Ion chromatography process of absorption solution]

Device: Dionex Integrion HPLC

Guard column Dionex Ionpac AS12A (4×50 mm)

Column: Dionex Ion Pac AS12A (4×200 mm)

Suppressor Dionex ADRS 600 (4 mm)

Eluent: sodium carbonate/sodium bicarbonate mixed solution

Detector: CD (electric conductivity detector)

[0069]

· Ion chromatography for extracted water

8 g of a sample was immersed in pure water, extraction was performed at 95℃ for 20 hours, and the extracted water was measured through ion chromatography.

Device: Dionex Integrion HPLC

Guard column Dionex Ionpac AS12A (4×50 mm)

Column: Dionex Ion Pac AS12A (4×200 mm)

Suppressor Dionex ADRS 600 (4 mm)

Eluent: sodium carbonate/sodium bicarbonate mixed solution

Detector: CD (electric conductivity detector)

[0070]

[Synthesis Example 1]

333 parts by weight of phenol and 0.5 parts by weight of concentrated hydrochloric acid were put into a flask including a stirrer, a reflux condenser, and a stirring device, stirred and dissolved, and then heated while blowing nitrogen, and 240 parts by weight of 4,4'-bischloromethylbiphenyl was continuously added over 4 hours while the temperature was maintained at 70℃. After the addition was completed, the reaction was additionally performed at the same temperature for 2 hours, and at 80℃ for an additional 2 hours. After the reaction was completed, excess phenol was distilled off by heating under a reduced pressure, and thereby 304 parts by weight of a phenolic resin (P1) was obtained. The obtained phenolic resin had a residual phenol content of 0.15%, a softening point of 133℃, and an ICI melt viscosity at 150℃ of 0.12 Pa·s. In the analysis through gel permeation chromatography, it was confirmed that n=1 was 40.5 area% (UV-254 nm).

[0071]

[Synthesis Example 2]

693 parts by weight of phenol, 0.006 parts by weight of paratoluenesulfonic acid and 75 parts by weight of sodium carbonate were put into a flask including a stirrer, a reflux condenser, and a stirring device, stirred and dissolved, and then heated while blowing nitrogen, and 799 parts by weight of 4,4'-bischloromethylbiphenyl was continuously added over 4 hours while the temperature was maintained at 105℃. After the addition was completed, the reaction was additionally performed at the same temperature for 1.5 hours. After the reaction was completed, 11.7 parts by weight of sodium tripolyphosphate was added and stirred for 30 minutes, and then heated under a reduced pressure to distill off excess phenol, and thereby 1,080 parts by weight of a

phenolic resin (P2) was obtained. The obtained phenolic resin had a residual phenol content of 0.01%, a softening point of 86.2℃, and an ICI melt viscosity at 150℃ of 0.53 Pa·s. In the analysis through gel permeation chromatography, it was confirmed that n=1 was 24.5 area% (UV-254 nm).

[0072]

[Example 1]

475 parts by weight of epichlorohydrin, 143 parts by weight of dimethyl sulfoxide, 0.76 parts by weight of dimethyl sulfide, and 0.06 parts by weight of dimethyl disulfide with respect to 200 parts by weight of the phenolic resin (P1) obtained in Synthesis Example 1 were put into a reaction container, and stirred and dissolved under a nitrogen atmosphere, and 42 parts by weight of flaky sodium hydroxide was then continuously added over 2 hours while the temperature was maintained at 45℃. After the addition of sodium hydroxide was completed, the reaction was performed at 45℃ for 2 hours and at 70℃ for an additional 1 hour. Next, washing with water was repeated to remove by-product salts and the like, excess epichlorohydrin and the like were then distilled off from the oil layer by heating under a reduced pressure, and 512 parts by weight of methyl isobutyl ketone was added to and dissolved in the residue. This methyl isobutyl ketone solution was heated at 70℃, and 20 parts by weight of a 30% sodium hydroxide aqueous solution was added and reacted for 1 hour, and washing of the reaction solution with water was then repeated until the washing solution became neutral. Next, methyl isobutyl ketone was distilled off from the oil layer by heating under a reduced pressure, and thereby 220 parts by weight of an epoxy resin mixture (EP1) was obtained. The obtained epoxy resin mixture had an epoxy equivalent of 276 g/eq., a softening point of 57.9℃, and an ICI melt viscosity of 0.09 Pa·s (150℃). It was confirmed that the sulfur content in the epoxy resin (EP1) was 24 ppm according to

quantification by a combustion method. In the analysis through gel permeation chromatography, it was confirmed that n=1 was 32.93 area% (UV-254 nm). In addition, as a result of ion chromatography for the extracted water (extracted at 95℃), it was confirmed that the quantitative value of sulfide ions was <1 ppm.

[0073]

[Example 2]

381 parts by weight of epichlorohydrin, 95.3 parts by weight of dimethyl sulfoxide, 0.65 parts by weight of dimethyl sulfide, and 0.78 parts by weight of dimethyl disulfide with respect to 200 parts by weight of the phenolic resin (P2) obtained in Synthesis Example 2 were put into a reaction container, and stirred and dissolved under a nitrogen atmosphere and 34.6 parts by weight of flaky sodium hydroxide was then continuously added over 2 hours while the temperature was maintained at 45℃. After the addition of sodium hydroxide was completed, the reaction was performed at 45℃ for 2 hours and at 70℃ for an additional 1 hour. Next, washing with water was repeated to remove by-product salts and the like, excess epichlorohydrin and the like were then distilled off from the oil layer by heating under a reduced pressure, and 444 parts by weight of methyl isobutyl ketone was added to and dissolved in the residue. This methyl isobutyl ketone solution was heated at 70℃, 8.2 parts by weight of a 30% sodium hydroxide aqueous solution was added and reacted for 1 hour, and washing of the reaction solution with water was then repeated until the washing solution became neutral. Next, methyl isobutyl ketone was distilled off from the oil layer by heating under a reduced pressure, and thereby 222 parts by weight of an epoxy resin mixture (EP2) was obtained. The obtained epoxy resin mixture had an epoxy equivalent of 292 g/eq., a softening point of 69℃, and an ICI melt viscosity of 0.31 Pa·s (150℃). The sulfur content in the epoxy resin (EP2) was 52 ppm according to quantification by a combustion

method. In the analysis through gel permeation chromatography, it was confirmed that n=1 was 22.1 area% (UV-254 nm). In addition, as a result of ion chromatography for the extracted water (extracted at 95℃), it was confirmed that the quantitative value of sulfide ions was <1 ppm.

[0074]

[Example 3]

381 parts by weight of epichlorohydrin, 95.3 parts by weight of dimethyl sulfoxide, 0.59 parts by weight of dimethyl sulfide, and 0.04 parts by weight of dimethyl disulfide with respect to 200 parts by weight of the phenolic resin (P2) obtained in Synthesis Example 2 were put into a reaction container, and stirred and dissolved under a nitrogen atmosphere, and 34.6 parts by weight of flaky sodium hydroxide was then continuously added over 2 hours while the temperature was maintained at 45℃. After the addition of sodium hydroxide was completed, the reaction was performed at 45℃ for 2 hours and at 70℃ for an additional 1 hour. Next, washing with water was repeated to remove by-product salts and the like, excess epichlorohydrin and the like were then distilled off from the oil layer by heating under a reduced pressure, and 444 parts by weight of methyl isobutyl ketone was added to and dissolved in the residue. This methyl isobutyl ketone solution was heated at 70℃, and 8.2 parts by weight of a 30% sodium hydroxide aqueous solution was added and reacted for 1 hour, and washing of the reaction solution with water was then repeated until the washing solution became neutral. Next, methyl isobutyl ketone was distilled off from the oil layer by heating under a reduced pressure, and thereby 215 parts by weight of an epoxy resin (EP3) was obtained. The obtained epoxy resin had an epoxy equivalent of 296 g/eq., a softening point of 69.8℃, and an ICI melt viscosity of 0.33 Pa·s (150℃). The sulfur content in the epoxy resin (EP3) was 19 ppm according to quantification by a combustion method. In the

analysis through gel permeation chromatography, it was confirmed that n=1 was 20.2 area% (UV-254 nm). In addition, as a result of ion chromatography for the extracted water (extracted at 95℃), it was confirmed that the quantitative value of sulfide ions was <1 ppm.

[0075]

[Comparative Example 1]

Synthesis was performed in the same manner as in Example 2 except that the amount of dimethyl sulfide and dimethyl disulfide was 0 parts by weight, and thereby 218 parts by weight of an epoxy resin (EP4) was obtained. The obtained epoxy resin mixture had an epoxy equivalent of 289 g/eq., a softening point of 67.1℃, and an ICI melt viscosity of 0.24 Pa·s (150℃). The sulfur content in the epoxy resin (EP4) was less than 5 ppm according to quantification by a combustion method. In the analysis through gel permeation chromatography, it was confirmed that n=1 was 21.5 area% (UV-254 nm). In addition, as a result of ion chromatography for the extracted water (extracted at 95℃), it was confirmed that the quantitative value of sulfide ions was <1 ppm.

[0076]

[Comparative Example 2]

381 parts by weight of epichlorohydrin, 45 parts by weight of dimethyl sulfoxide, and 5 parts by weight of butanol with respect to 200 parts by weight of the phenolic resin (P2) obtained in Synthesis Example 2 were put into a reaction container, and stirred and dissolved under a nitrogen atmosphere, and 39 parts by weight of flaky sodium hydroxide was then continuously added over 2 hours while the temperature was maintained at 45℃. After the addition of sodium hydroxide was completed, the reaction was performed at 45℃ for 2 hours and at 70℃ for an additional 1 hour. Next,

washing with water was repeated to remove by-product salts and the like, excess epichlorohydrin and the like were then distilled off from the oil layer by heating under a reduced pressure, and 444 parts by weight of methyl isobutyl ketone was added to and dissolved in the residue. This methyl isobutyl ketone solution was heated at 70℃, 10 parts by weight of a 30% sodium hydroxide aqueous solution was added and reacted for 1 hour, and washing of the reaction solution with water was then repeated until the washing solution became neutral. Next, methyl isobutyl ketone was distilled off from the oil layer by heating under a reduced pressure, and thereby 211 parts by weight of an epoxy resin (EP5) was obtained. The obtained epoxy resin had an epoxy equivalent of 312 g/eq., a softening point of 66.9℃, and an ICI melt viscosity of 0.25 Pa·s (150℃). The sulfur content in the epoxy resin (EP5) was less than 5 ppm according to quantification by a combustion method. In the analysis through gel permeation chromatography, it was confirmed that n=1 was 21.4 area% (UV-254 nm). In addition, as a result of ion chromatography for the extracted water (extracted at 95℃), it was confirmed that the quantitative value of sulfide ions was <1 ppm.

[0077]

[Examples 4, 5, and 6 and Comparative Example 3]

The epoxy resins (EP1, EP2, and EP3), the comparative epoxy resin (EP5) were used as main agents, phenol novolac (abbreviation; PN, hydroxyl group equivalent of 106 g/eq.) was used as a curing agent, and triphenylphosphine (abbreviation; TPP) was used as a curing accelerator, and these were added at weight ratios shown in the formulation composition in Table 1, kneaded with two rollers, and formed into tablets, and a resin molded component was then prepared by transfer molding, and cured under curing conditions of 160℃ for 2 hours and 180℃ for an additional 6 hours.

[0078]

Physical property values were measured under the following conditions

·3-point bending test

Manufacturer: commercially available from A&D Co., Ltd.

Device: RTG-1310

Test rate: 3 mm/min

Distance between fulcrums: 64 mm

Measurement temperature 30℃

Fig. 1 shows a stress-strain diagram when the 3-point bending test was performed.

[0079]

[Table 1]

		Name	Example 4	Example 5	Example 6	Comparative Example 3
Formulation composition	Epoxy resin	EP1	100			
		EP2		100		
		EP3			100	
		EP5				100
	Curing agent	PN	38	36	36	34
	Curing accelerator	TPP	1	1	1	1
Physical property data	30℃ maximum point stress	MPa	97	118	113	91
	30℃ strain	%	4.3	7.1	5.2	3.7

[0080]

[Examples 7, 8, and 9 and Comparative Example 4]

The epoxy resins (EP1, EP2, and EP3) and the comparative epoxy resin (EP5) were used as main agents, phenol novolac (abbreviation; PN, hydroxyl group equivalent of 103 g/eq.) was used as a curing agent, and triphenylphosphine (abbreviation; TPP) was used as a curing accelerator, and these were added at weight ratios shown in the formulation composition in Table 2, kneaded with two rollers, and formed into tablets, and a resin molded component was then prepared by transfer molding, and cured under

curing conditions of 160℃ for 2 hours and 180℃ for an additional 6 hours.

[0081]

Physical property values were measured under the following conditions.

·3-point bending test

Manufacturer: commercially available from A&D Co., Ltd.

Device: RTG-1310

Test rate: 3 mm/min

Distance between fulcrums: 64 mm

Measurement temperature 120℃

Fig. 2 shows a stress-strain diagram when the 3-point bending test was performed.

[0082]

[Table 2]

		Name	Example 7	Example 8	Comparative Example 4	Comparative Example 5
Formulation composition	Epoxy resin	EP2	100			
		EP3		100		
		EP4			100	
		EP5				100
	Curing agent	PN	35	35	35	33
	Curing accelerator	TPP	1	1	1	1
Physical property data	120℃ maximum point stress	MPa	67	66	61	59
	120℃ strain	%	8.9	6.0	5.5	6.4

[0083]

Based on the results in Table 1 and Fig. 1, it was confirmed that Examples 4 to 6 had excellent maximum point stress and strain at 30℃. In addition, based on the results in Table 2 and Fig. 2, it was confirmed that Examples 7 and 8 had excellent maximum

point stress and strain at 120℃. Particularly, it was confirmed that Examples 5 and 7, which had a large sulfur amount, had particularly excellent maximum point stress and strain at both 30℃ and 120℃.

[0084]

That is, it was confirmed that the epoxy resin mixture of the present invention can be formed into a cured product exhibiting excellent mechanical strength and toughness at room temperature and in a high temperature range.

[Industrial Applicability]

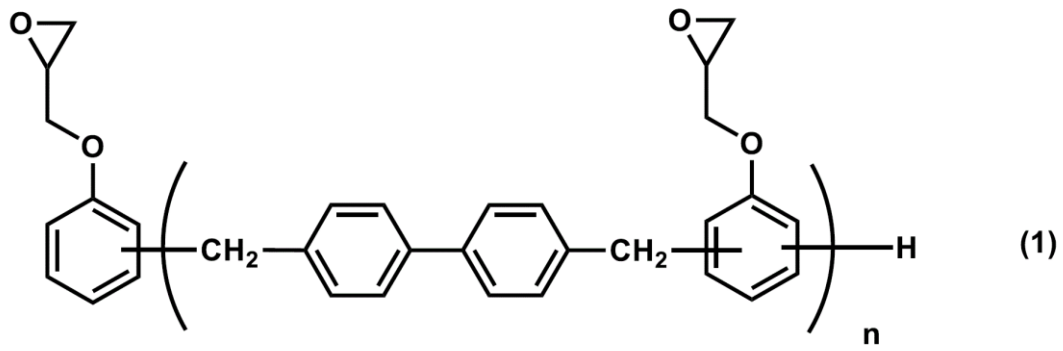
[0085]

The present invention is beneficial for applications such as insulating materials for electrical and electronic components (highly reliable semiconductor encapsulating materials, etc.), laminated substrates (printed wiring substrates, build-up substrates, etc.), various composite materials such as FRP, adhesives, and paints, and specifically, laminated substrates, and is beneficial for metal foil clad laminated substrates, insulating materials for build-up substrates, flexible substrate materials and the like.

[CLAIMS]

[Claim 1]

An epoxy resin mixture, containing an epoxy resin represented by the following Formula (1) and having a sulfur content of 15 ppm to 400 ppm obtained by a combustion method:

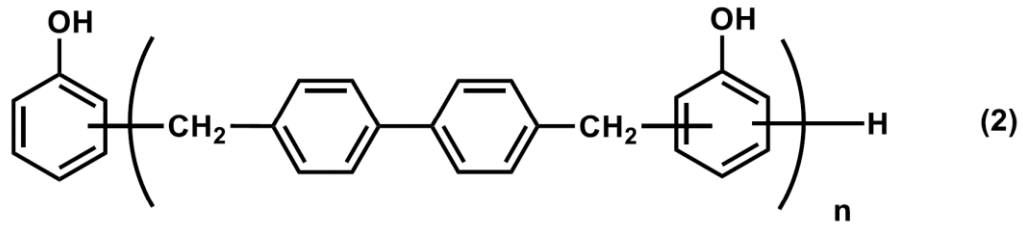


(1)

(in Formula (1), n is the number of repetitions and represents a real number of 1 to 20).

[Claim 2]

An epoxy resin mixture, obtained by reacting a phenolic resin represented by the following Formula (2), epichlorohydrin, and a sulfur-containing compound:



(2)

(in Formula (2), n is the number of repetitions and represents a real number of 1 to 20).

[Claim 3]

An epoxy resin composition, containing the epoxy resin mixture according to claim 1 or 2, and a curing agent.

[Claim 4]

A cured product, obtained by curing the epoxy resin composition according to claim 3.