

Description

Title of Invention: EPOXY RESIN COMPOSITION AND CURED PRODUCT

Technical Field

[0001] The present invention relates to an epoxy resin composition that provides a cured product excellent in low dielectric property and flame retardancy, and also excellent in low water-absorbing property and the like, and to a cured product of the composition.

Background Art

[0002] In recent years, development of a base resin having additionally high performance has been required in association with progress of, in particular, an advanced material field. For example, in a semiconductor sealing field, a problem of a package crack has become serious owing to thinning, and an increase in area, of a package corresponding to high-density packaging in recent years, and widespread use of a surface packaging system. Accordingly, the base resin has been strongly required to have improved moisture resistance, heat resistance, adhesive property with a metal base material, and the like. In addition, in a printed wiring board field, multilayering, thinning, fine-pitching of a circuit, and the like have been performed in recent years in order that a large amount of information may be processed at a high speed. However, a wiring board material additionally excellent in dielectric characteristic

has been required in order that processing having an additionally high speed may be realized. Further, from the viewpoint of reducing an environmental load, there has been a trend toward elimination of a halogen-based flame retardant and hence a base resin additionally excellent in flame retardancy has been required.

[0003] However, out of the related-art epoxy resin-based materials, a material that sufficiently satisfies those requirements has still been unknown. For example, a well-known bisphenol-type epoxy resin has been widely used because the resin is liquid at normal temperature and hence excellent in workability, and because the resin can be easily mixed with a curing agent, an additive, or the like. However, the resin involves problems in terms of its heat resistance and moisture resistance. In addition, a phenol novolac-type epoxy resin has been known as a resin improved in heat resistance, but involves problems in terms of its moisture resistance and impact resistance. In addition, Patent Literature 1 proposes an epoxy compound of a phenol aralkyl resin intended for improvements in moisture resistance and impact resistance, but its heat resistance and flame retardancy are not sufficient.

[0004] Patent Literatures 2, 3, and the like each disclose a method involving adding a phosphate-based flame retardant as measures to improve flame retardancy without using any halogen-based flame retardant. However, the method involving using the phosphate-based flame retardant does not provide sufficient moisture resistance. In addition, the method involves a problem in that a

phosphate hydrolyzes under a high-temperature and high-humidity environment to reduce its reliability as an insulating material.

[0005] Patent Literature 4 discloses a phosphorus-containing epoxy resin composition as measures to improve flame retardancy without using any phosphate-based flame retardant, and when the composition is applied as a matrix resin for a laminated plate, excellent flame retardancy is expressed without any reduction in insulation reliability. However, the phosphorus-containing epoxy resin adopts a polarized structure resulting from a phosphate structure and hence its low dielectric property has not been sufficient.

[0006] Patent Literatures 5, 7, and 8 each disclose an example in which an aralkyl-type epoxy resin having a biphenyl structure is applied as a resin for improving flame retardancy that is free of any halogen atom to a semiconductor-sealing material. Patent Literature 6 discloses an example in which an aralkyl-type epoxy resin having a naphthalene structure is used. However, the performance of each of those epoxy resins is insufficient in terms of one of flame retardancy, moisture resistance, and heat resistance. It should be noted that Patent Literatures 9 and 10 each disclose a naphthol-based aralkyl-type epoxy resin and a semiconductor-sealing material containing the resin, but none of the resin and the material pays attention to flame retardancy.

[0007] Further, Patent Literature 11 discloses an epoxy resin composition containing a styrenated phenol novolac-type epoxy resin

as an example paying attention to improvements in low water-absorbing property and low stress property, but the composition does not pay attention to flame retardancy. Meanwhile, Patent Literature 12 discloses an epoxy resin composition containing the same styrenated phenol novolac-type epoxy resin as an example paying attention to an improvement in dielectric characteristic, but the composition has not achieved compatibility between flame retardancy and a dielectric characteristic.

Citation List

Patent Literature

[0008]

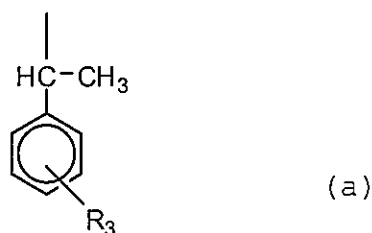
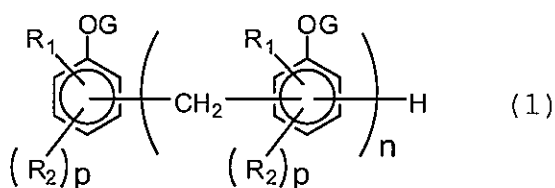
- [PTL 1] JP 63-238122 A
- [PTL 2] JP 09-235449 A
- [PTL 3] JP 10-182792 A
- [PTL 4] JP 11-279258 A
- [PTL 5] JP 11-140166 A
- [PTL 6] JP 2004-59792 A
- [PTL 7] JP 04-173831 A
- [PTL 8] JP 2000-129092 A
- [PTL 9] JP 03-90075 A
- [PTL 10] JP 03-281623 A
- [PTL 11] JP 08-120039 A
- [PTL 12] JP 05-140265 A

Summary of Invention

Technical Problem

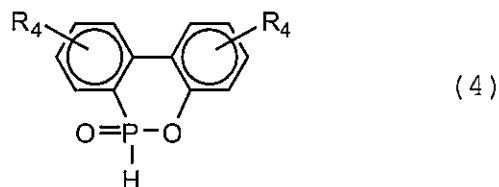
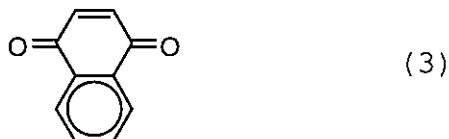
[0009] Therefore, an object of the present invention is to provide an epoxy resin composition that secures flame retardancy in the absence of a halogen, has excellent performance in terms of low dielectric property, flame retardancy, and the like, and is useful in an application such as lamination, molding, casting, or adhesion, and a cured product of the composition.

[0010] That is, the present invention relates to an epoxy resin composition, including: epoxy resins; a curing agent; and an inorganic filler, in which: the epoxy resins include, as epoxy resin components, an epoxy resin represented by the following general formula (1) and a phosphorus-containing epoxy resin having a phosphorus content of from 0.5 to 5.0 wt%; and the content of the epoxy resin represented by the following general formula (1) is 30 wt% or more and the content of the phosphorus-containing epoxy resin is 30 wt% or more with respect to the entirety of the epoxy resins:



(wherein G represents a glycidyl group, R_1 represents hydrogen or a hydrocarbon group having 1 to 6 carbon atoms, R_2 represents a substituent represented by the formula (a), n represents a number of from 1 to 20, p represents a number of from 0.1 to 2.5, and R_3 represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms.)

[0011] In addition, the present invention relates to an epoxy resin composition, in which the phosphorus-containing epoxy resin includes a phosphorus-containing epoxy resin obtained by causing an epoxy resin having two or more epoxy groups per molecule, a quinone compound represented by the following formula (2) or (3), and a phosphorus compound having one active hydrogen bonded to a phosphorus atom represented by the following formula (4) to react with one another:



(wherein R_4 represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms.)

[0012] Further, the present invention relates to an epoxy resin

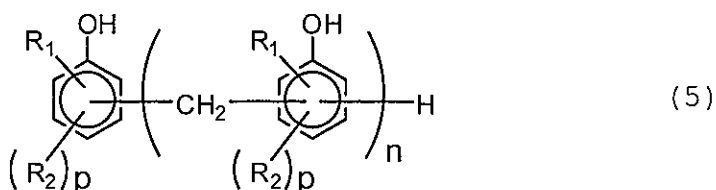
composition, in which the inorganic filler includes a fibrous glass base material, and an epoxy resin cured product, which is obtained by curing the epoxy resin composition.

Description of Embodiments

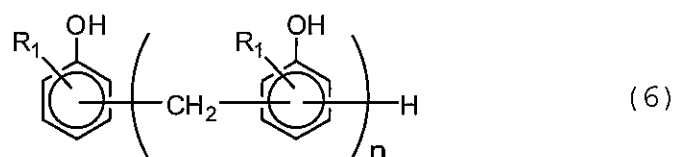
[0013] An epoxy resin composition of the present invention contains, as essential components, two kinds of epoxy resin components, a curing agent component, and an inorganic filler. The composition contains desirably 50 wt% or more, more preferably 80 wt% or more, still more preferably 95 wt% or more of those essential components.

[0014] First, an epoxy resin represented by the general formula (1) as a first epoxy resin component in the epoxy resin composition of the present invention is described. The epoxy resin represented by the general formula (1) is obtained by epoxidizing a styrene-added polyhydric hydroxy resin represented by the general formula (5). In addition, the styrene-added polyhydric hydroxy resin (also referred to as "StPN") represented by the general formula (5) can be obtained by subjecting a polyhydric hydroxy compound represented by the general formula (6) (also referred to as "polyhydric hydroxy compound (6)") and a styrene to an addition reaction.

[0015]



(R₁ represents hydrogen or a hydrocarbon group having 1 to 6 carbon atoms, R₂ represents a substituent represented by the formula (a), n represents a number of from 1 to 20, and p represents a number of from 0.1 to 2.5.)



(Wherein, R₁ represents hydrogen or a hydrocarbon group having 1 to 6 carbon atoms, and n represents a number of from 1 to 20.)

[0016] The hydroxyl equivalent of the styrene-added polyhydric hydroxy resin represented by the general formula (5) can be arbitrarily adjusted by first adding the styrene to the basic structure of the polyhydric hydroxy compound (6). Herein, the phrase "adding the styrene" means that hydrogen of a benzene ring of the polyhydric hydroxy compound (6) is substituted with a substituent represented by the formula (a) (also referred to as "styrenyl group").

[0017] In other words, adding styrene rich in aromaticity improves the aromaticity of the epoxy resin, which is effective in improving its dielectric characteristic. That is, introducing a styrenyl group as a hydrocarbon group having low polarity into an epoxy resin structure relatively reduces a polar group concentration and hence can provide an epoxy resin additionally excellent in low dielectric property.

[0018] Accordingly, an epoxy resin composition excellent in low dielectric property, in particular, an epoxy resin composition

for a printed wiring board is obtained by using such resin. That is, excellent physical properties including excellent low dielectric property and excellent flame retardancy, and excellent low water-absorbing property are expressed in such composition, and high-reliability sealing of electrical and electronic parts, a high-reliability circuit substrate material, or the like is achieved by using the material.

[0019] The StPN is obtained by subjecting the polyhydric hydroxy compound (6) represented by the general formula (6) and the styrene to an addition reaction. At this time, a ratio between the polyhydric hydroxy compound (6) and the styrene is as follows in consideration of a balance between the flame retardancy and curability of a cured product to be obtained: the use ratio of the styrene with respect to 1 mol of a hydroxy group of the polyhydric hydroxy compound falls within the range of preferably from 0.1 to 2.5 mol, more preferably from 0.1 to 1.0 mol, still more preferably from 0.3 to 0.8 mol. When the ratio falls short of the range, a state in which the properties of the polyhydric hydroxy compound as a raw material remain unimproved is established, and when the ratio exceeds the range, a functional group density becomes so low that the curability tends to reduce. In addition, the reaction is preferably performed in the presence of an acid catalyst.

[0020] In the general formulae (5) and (6), and the general formula (1), common symbols have the same meaning. R_1 represents a styrenyl group represented by the formula (a). p , which represents

a number of from 0.1 to 2.5, means the average number (number average) of styrenyl groups with which one phenol ring is substituted. p represents a number of preferably from 0.1 to 2, more preferably from 0.1 to 1.0, still more preferably from 0.3 to 1, yet still more preferably from 0.3 to 0.8. It should be noted that phenol rings at both terminals can each be substituted with a maximum of four styrenyl groups and an intermediate phenol ring can be substituted with a maximum of three styrenyl groups, and hence when n represents 1, the epoxy resin can be substituted with a maximum of eight styrenyl groups.

From another viewpoint, the substitution number (number average) of styrenyl groups per molecule of the StPN to be used in the present invention is preferably 1 or more, more preferably 2 or more, still more preferably from 2.6 to 4.

[0021] In the formula (a), R_3 represents hydrogen or a hydrocarbon group having 1 to 6 carbon atoms, preferably hydrogen or an alkyl group having 1 to 3 carbon atoms, more preferably hydrogen. R_3 is determined by the styrene to be used as a reaction raw material.

[0022] In the general formula (1), n represents a number of from 1 to 20, preferably a number in the range of from 1.5 to 5.0 in terms of a number average.

[0023] A phenol to be used for obtaining the polyhydric hydroxy compound (6) is phenol or a phenol substituted with a hydrocarbon group having 1 to 6 carbon atoms, preferably phenol or a phenol substituted with an alkyl group having 1 to 4 carbon atoms, more

preferably phenol. When phenol is used as the phenol, the phenol may contain a small amount of any other phenol component. Examples thereof include o-cresol, m-cresol, p-cresol, an ethylphenol, an isopropylphenol, a tert-butylphenol, an allylphenol, a phenylphenol, 2,6-xylenol, 2,6-diethylphenol, hydroquinone, resorcin, catechol, 1-naphthol, 2-naphthol, 1,5-naphthalenediol, 1,6-naphthalenediol, 1,7-naphthalenediol, 2,6-naphthalenediol, and 2,7-naphthalenediol. The phenol may contain two or more kinds of those phenols and naphthols.

[0024] The styrene to be used in the reaction with the polyhydric hydroxy compound is styrene or styrene substituted with a hydrocarbon group having 1 to 6 carbon atoms, preferably styrene. The styrene may contain a small amount of any other reactive component, and in the case where styrene is used as the styrene, the styrene can contain an unsaturated bond-containing component such as α -methylstyrene, divinylbenzene, indene, coumarone, benzothiophene, indole, or vinyl naphthalene as the other reactive component. In this case, the polyhydric hydroxy compound to be obtained contains a compound in which an aromatic ring is substituted with a group produced from such component.

[0025] The reaction between the polyhydric hydroxy compound and the styrene can be performed in the presence of the acid catalyst, and the catalyst is used in an amount in the range of from 10 to 1,000 ppm, preferably from 100 to 500 ppm. When the amount exceeds the range, a methylene crosslinkage of the polyhydric hydroxy

compound (6) is liable to cleave, and a monohydric phenol component produced as a byproduct by the cleavage reaction reduces the curability and heat resistance of the epoxy resin. On the other hand, when the amount falls short of the range, reactivity reduces and hence a large amount of an unreacted styrene monomer remains.

[0026] The acid catalyst can be appropriately selected from well-known inorganic acids and organic acids. Examples thereof include: a mineral acid such as hydrochloric acid, sulfuric acid, or phosphoric acid; an organic acid such as formic acid, oxalic acid, trifluoroacetic acid, p-toluenesulfonic acid, dimethyl sulfate, or diethyl sulfate; a Lewis acid such as zinc chloride, aluminum chloride, iron chloride, or boron trifluoride; and a solid acid such as an ion exchange resin, active clay, silica-alumina, or zeolite.

[0027] In addition, the reaction is performed at a reaction temperature in the range of from 40 to 120°C. When the temperature falls short of the range, the reactivity reduces and hence a reaction time lengthens. In addition, when the temperature exceeds the range, part of the methylene crosslinkages of the polyhydric hydroxy compound (6) are liable to cleave, and the monohydric phenol component produced as a byproduct by the cleavage reaction reduces the curability and the heat resistance.

[0028] In addition, the reaction is typically performed for from 1 to 20 hr. Further, in the reaction, as a solvent, there may be used, for example: an alcohol such as methanol, ethanol, propanol,

butanol, ethylene glycol, methyl cellosolve, or ethyl cellosolve; a ketone such as acetone, methyl ethyl ketone, or methyl isobutyl ketone; an ether such as dimethyl ether, diethyl ether, diisopropyl ether, tetrahydrofuran, or dioxane; or an aromatic compound such as benzene, toluene, chlorobenzene, or dichlorobenzene.

[0029] A specific method of performing the reaction is generally a method involving collectively loading all raw materials and causing the raw materials to react with each other as they are at a predetermined temperature, or a method involving loading the polyhydric hydroxy compound and the catalyst, and causing the styrene to react with the compound while maintaining a predetermined temperature and dropping the styrene. At this time, a drop time is preferably 5 hr or less, typically from 1 to 10 hr. After the reaction, when a solvent is used, the resin to be used in the present invention can be obtained by removing the solvent by distillation as required after the removal of the catalyst component, or when the solvent is not used, the target product can be obtained through direct discharge during a hot state.

[0030] The epoxy resins to be used in the present invention are the epoxy resin represented by the general formula (1) and a phosphorus-containing epoxy resin having a phosphorus content of from 1.0 to 5.0 wt%.

Hereinafter, the epoxy resin represented by the general formula (1) is sometimes abbreviated as "StPNE" and the phosphorus-containing epoxy resin having a phosphorus content of

from 1.0 to 5.0 wt% is sometimes referred to as "phosphorus-containing epoxy resin." The StPNE can be obtained by epoxidizing the StPN.

[0031] In the general formula (1), G represents a glycidyl group, which is produced by the reaction of a hydroxyl group of the general formula (5), and R₁ represents a styrenyl group.

[0032] Although it is advantageous to produce the StPNE to be used in the present invention by causing the StPN represented by the general formula (3) and epichlorohydrin to react with each other, a method for the production is not limited to the reaction.

[0033] In addition to the reaction in which the StPN is caused to react with epichlorohydrin, a method involving causing the StPN and an allyl halide to react with each other to provide an allyl ether compound and then causing the compound to react with a peroxide can also be adopted. The reaction in which the StPN is caused to react with epichlorohydrin can be performed in the same manner as in a typical epoxidation reaction.

[0034] For example, the following method is adopted: after the StPN has been dissolved in an excess amount of epichlorohydrin, the solution is subjected to a reaction in the presence of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide at a temperature in the range of from 20 to 150°C, preferably from 30 to 80°C for from 1 to 10 hr. The usage of the alkali metal hydroxide at this time falls within the range of from 0.8 to 1.5 mol, preferably from 0.9 to 1.2 mol with respect to 1 mol of a hydroxyl group of the StPN. In addition, epichlorohydrin, which is used in an excess

amount with respect to 1 mol of the hydroxyl group in the StPN, is used in an amount in the range of from 1.5 to 30 mol, preferably from 2 to 15 mol with respect to 1 mol of the hydroxyl group in the StPN in ordinary cases. After the completion of the reaction, the excess amount of epichlorohydrin is removed by distillation, the residue is dissolved in a solvent such as toluene or methyl isobutyl ketone and filtered, and an inorganic salt is removed by washing the filtrate with water, followed by the removal of the solvent by distillation. Thus, the target epoxy resin can be obtained.

[0035] The epoxy resin composition of the present invention contains 30 wt% or more, preferably 30 to 70 wt%, more preferably 40 to 60 wt% of the epoxy resin represented by the general formula (1) in all the epoxy resin components.

[0036] The epoxy resin composition of the present invention uses the phosphorus-containing epoxy resin having a phosphorus content of from 1.0 to 5.0 wt% as a second epoxy resin component. The content of the phosphorus-containing epoxy resin in all the epoxy resin components is 30 wt% or more, preferably from 30 to 70 wt%, more preferably from 40 to 60 wt%. When the content exceeds the range, the low dielectric property of the composition reduces, and when the content falls short of the range, its flame retardancy is not sufficiently expressed.

[0037] The phosphorus content of the phosphorus-containing epoxy resin is from 1.0 to 5.0 wt%, preferably from 2.0 to 4.0 wt%.

When the phosphorus content is less than 1.0 wt%, the flame retardancy is not sufficiently expressed, and when the content is more than 5.0 wt%, the content of a phosphate structure having a high dielectric constant increases and hence the expression of the low dielectric property cannot be expected.

[0038] Preferably used as the phosphorus-containing epoxy resin is a phosphorus-containing epoxy resin obtained by causing an epoxy resin having two or more epoxy groups per molecule, a quinone compound represented by the formula (2) or (3), and a phosphorus compound having one active hydrogen bonded to a phosphorus atom represented by the formula (4) to react with one another. In the formula (4), R_4 , which is selected from a hydrogen atom and a hydrocarbon group having 1 to 6 carbon atoms, preferably represents a hydrogen atom.

[0039] In this case, although the epoxy resin having two or more epoxy groups per molecule may be a single resin, or may be a mixture of two or more kinds of resins, a novolac-type epoxy resin is present at a content of preferably 20 wt% or more, more preferably 40 wt% or more in the epoxy resin to be used in the phosphorus-containing epoxy resin. When the content of the novolac-type epoxy resin is less than 20 wt%, the flame retardancy and heat resistance of the phosphorus-containing epoxy resin are liable to deteriorate. When the epoxy resin is a mixture, a resin except the novolac-type epoxy resin is exemplified by, but not limited to, resins each having two or more epoxy groups per molecule such

as a bisphenol-type epoxy resin, a resorcin-type epoxy resin, a polyglycol-type epoxy resin, and a fluorene-type epoxy resin.

[0040] A resin that can be preferably used as the phosphorus-containing epoxy resin to be used in the present invention is exemplified by, but not limited to, resins known to the public by Patent Literature 4 and JP 2000-309623 A. Such a phosphorus-containing epoxy resin that halogen-free flame retardation is achieved by introducing a phosphorus atom into its resin skeleton is preferred. Specific examples thereof include EPOTOHTO FX-305 (manufactured by Nippon Steel Chemical Co., Ltd.) and EPOTOHTO FX-289B (manufactured by Nippon Steel Chemical Co., Ltd.).

[0041] The epoxy resin composition of the present invention, which uses the epoxy resin components, i.e., the epoxy resin represented by the general formula (1) and the phosphorus-containing epoxy resin as essential epoxy resins, can use any other epoxy resin in combination to the extent that the object of the present invention is not impaired.

[0042] Examples of such other epoxy resin include: an epoxidized product of a dihydric phenol such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 2,2'-biphenol, resorcin, or a naphthalenediol; an epoxidized product of a tri- or more hydric phenol such as tris(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, or o-cresol novolac; an epoxidized product of a cocondensed resin of

dicyclopentadiene and a phenol; an epoxidized product of a phenol aralkyl resin synthesized from, for example, a phenol and p-xylylene dichloride; an epoxidized product of a biphenyl aralkyl-type phenol resin synthesized from, for example, a phenol and bis(chloromethyl)biphenyl; and an epoxidized product of a naphthol aralkyl resin synthesized from, for example, a naphthol and p-xylylene dichloride. One kind of those epoxy resins may be used alone, or two or more kinds thereof may be used in combination. Although the compounding amount of any such resin is not limited as long as the object of the present invention is not impaired, the compounding amount is less than 50 wt% with respect to the sum of the StPNE and the phosphorus-containing epoxy resin.

[0043] All curing agents generally known as curing agents for epoxy resins can each be used as the curing agent to be used in the epoxy resin composition of the present invention. Examples thereof include dicyandiamide, polyhydric phenols, acid anhydrides, and aromatic and aliphatic amines.

[0044] Specific examples of the amine-based curing agent to be used in the epoxy resin composition of the present invention include: an aromatic amine such as 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenyl sulfone, m-phenylenediamine, or p-xylylenediamine; and an aliphatic amine such as ethylenediamine, hexamethylenediamine, diethylenetriamine, or triethylenetetramine.

[0045] In addition, specific examples of the phenol-based

curing agent include: a dihydric phenol such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, catechol, or a naphthalenediol; a tri- or more hydric phenol typified by, for example, tris(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, o-cresol novolac, naphthol novolac, or polyvinyl phenol; and a polyhydric phenolic compound synthesized through a reaction of a phenol, a naphthol, or a dihydric phenol such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, catechol, or a naphthalenediol and a crosslinking agent such as formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, p-xylylene glycol, p-xylylene glycol dimethyl ether, divinylbenzene, diisopropenylbenzene, a dimethoxymethylbiphenyl, divinylbiphenyl, or a diisopropenylbiphenyl.

[0046] Examples of the acid anhydride include phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methylhimic anhydride, nadic anhydride, and trimellitic anhydride.

[0047] With regard to a compounding ratio between the epoxy resins and curing agent in the epoxy resin composition of the present invention, an equivalent ratio between an epoxy group and a functional group in the curing agent preferably falls within the range of from

0.8 to 1.5. When the ratio deviates from the range, an unreacted epoxy group or functional group in the curing agent remains even after curing, and hence the reliability and physical properties such as a water absorption coefficient of the composition when turned into a cured product reduce.

[0048] Further, a known curing accelerator can be used in the epoxy resin composition of the present invention as required. Examples thereof include amines, imidazoles, organic phosphines, and Lewis acids. The addition amount thereof typically falls within the range of from 0.2 to 5 parts by weight with respect to 100 parts by weight of the epoxy resins.

[0049] Examples of the filler to be used in the present invention include a fibrous filler such as a glass fiber, a carbon fiber, or an aramid fiber; and an inorganic filler such as silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, fosterite, steatite, spinel, mullite, or titania. One kind of those fillers may be used alone, or two or more kinds thereof may be used in combination. However, it is preferred that a glass fiber be used as a main component thereof.

[0050] In addition, as required, an oligomer or polymer compound such as polyester, polyamide, polyimide, polyether, polyurethane, a petroleum resin, an indene-coumarone resin, or a phenoxy resin may be appropriately compounded in the epoxy resin composition of the present invention, or an additive such as a pigment, a flame

retardant, a thixotropy-imparting agent, a coupling agent, or a flowability improver may be compounded therein. Examples of the pigment include an organic or inorganic extender pigment and a flaky pigment. Examples of the thixotropy-imparting agent can include a silicone-based thixotropy-imparting agent, a castor oil-based thixotropy-imparting agent, an aliphatic amide wax, an oxidized polyethylene wax, and an organic bentonite-based thixotropy-imparting agent. In addition, curing accelerators such as amines, imidazoles, organic phosphines, and Lewis acids may each be compounded therein as required. The compounding amount of any such accelerator is typically from 0.2 to 5 parts by weight with respect to 100 parts by weight of the epoxy resins. Further, the resin composition of the present invention can be compounded with, for example, a release agent such as a carnauba wax or an OP wax, a coupling agent such as γ -glycidoxypropyltrimethoxysilane, a colorant such as carbon black, a flame retardant such as antimony trioxide, a stress-lowering agent such as a silicone oil, or a lubricant such as calcium stearate as required.

[0051] The epoxy resin composition of the present invention can be generally obtained by: sufficiently mixing predetermined compounding amounts of compounding components such as the epoxy resins and the curing agent component with a mixer or the like; then kneading the mixture with a mixing roll, an extruder, or the like; cooling the kneaded product; and pulverizing the cooled product.

[0052] Alternatively, a varnish-like epoxy resin composition can be obtained by dissolving the compounding components in: an aromatic solvent such as benzene, toluene, xylene, or chlorobenzene; a ketone-based solvent such as acetone, methyl ethyl ketone, methyl isobutyl ketone, or cyclohexanone; an aliphatic hydrocarbon solvent such as hexane, heptane, or methylcyclohexane; an alcohol solvent such as ethanol, isopropanol, butanol, or ethylene glycol; an ether-based solvent such as diethylether, dioxane, tetrahydrofuran, or diethylene glycol dimethyl ether; or a polar solvent such as N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, or N-methylpyrrolidone. A prepreg-like epoxy composition can be obtained by impregnating the varnish-like epoxy resin composition into a fibrous filler such as a glass fiber, a carbon fiber, or an aramid fiber, and then drying the resultant to remove the organic solvent. When the prepreg-like epoxy composition is produced, a fibrous glass base material is preferably used. In this case, the fibrous glass base material may be a cloth or the like.

[0053] In order that a cured product may be obtained by using the epoxy resin composition of the present invention, a method such as transfer molding, press molding, cast molding, injection molding, or extrusion molding is applied. In addition, a method such as vacuum pressing is adopted as an approach to curing the prepreg-like epoxy resin composition. A temperature at this time typically falls within the range of from 120 to 220°C.

[0054] A cured product of the present invention can be obtained

through the curing of the epoxy resin composition by a molding method such as casting, compression molding, or transfer molding. The temperature at which the cured product is produced is typically from 120 to 220°C.

Examples

[0055] Hereinafter, the present invention is specifically described on the basis of Synthesis Examples, Examples, and Comparative Examples.

[0056] Synthesis Example 1

(Synthesis of polyhydric hydroxy resin)

105 g of phenol novolac (manufactured by Showa Highpolymer Co., Ltd.; BRG-555, hydroxyl equivalent: 105 g/eq., softening point: 67°C, melt viscosity at 150°C: 0.08 Pa·s, n: 3.3 on average) as a polyhydric hydroxy compound component, 5.3 g of toluene, and 0.061 g (300 ppm) of p-toluenesulfonic acid as an acid catalyst were loaded into a 1-L four-necked flask, and the temperature of the mixture was increased to 100°C. Next, while the mixture was stirred at 100°C, 94 g (0.9 mol) of styrene were dropped to the mixture over 3 hr, and the resultant mixture was subjected to a reaction. After the mixture had been further subjected to a reaction at 100°C for 2 hr, 0.054 g of 30% Na₂CO₃ was added to neutralize the resultant. Next, the neutralized product was dissolved in 369 g of MIBK and the solution was washed with water at 80°C five times. Subsequently, MIBK was removed by distillation under reduced pressure. After that,

191 g of a polyhydric hydroxy resin were obtained. The resin had a hydroxyl equivalent of 199 g/eq., a softening point of 77°C, a melt viscosity at 150°C of 0.15 Pa·s, and a p of 0.9. The resin is referred to as "StPN-A".

[0057] Synthesis Example 2

(Synthesis of epoxy resin)

150 g of the StPN-A obtained in Synthesis Example 1, 419 g of epichlorohydrin, and 63 g of diethylene glycol dimethyl ether were loaded into a four-necked separable flask, and the contents were stirred and dissolved. After the contents had been uniformly dissolved, under a reduced pressure of 130 mmHg, the temperature of the solution was kept at 65°C and 62.9 g of a 48% aqueous solution of sodium hydroxide were dropped to the solution over 4 hr. Water distilled out by reflux during the dropping and epichlorohydrin were separated from each other with a separating tank, epichlorohydrin was returned to the reaction vessel, and water was removed to the outside of the system, followed by a reaction. After the completion of the reaction, a produced salt was removed by filtration. Further, the residue was washed with water and then epichlorohydrin was removed by distillation. Thus, 180 g of an epoxy resin were obtained. The resultant resin had an epoxy equivalent of 270 g/eq., a softening point of 61°C, a melt viscosity at 150°C of 0.13 Pa·s, an n of 3.3 on average, and a p of 0.9. The resin is referred to as "StPNE-A".

[0058] Examples 1 to 4 and Comparative Examples 1 to 4

An epoxy resin varnish was prepared by dissolving the epoxy resin (StPNE-A) obtained in Synthesis Example 2, a phosphorus-containing epoxy resin, curing agent, and inorganic filler described below, and 2-ethyl-4-methylimidazole as a curing accelerator in a solvent according to a compounding ratio shown in each of Tables 1 and 2. Numerical values in the tables each represent a compounding amount in the unit of part(s) by weight. After that, the epoxy resin varnish was impregnated into a glass cloth so that their weight ratio after drying became 1:1, followed by the removal of the solvent by drying. Thus, a prepreg was obtained. Four prepregs were laminated and subjected to hot pressing to provide a cured product of a laminated plate. After that, the cured product was subjected to the measurement of various physical properties. Tables 3 and 4 show the results.

[0059] An epoxy resin A "FX-289B (manufactured by Nippon Steel Chemical Co., Ltd., epoxy equivalent: 305 g/eq., phosphorus content: 2.0 wt%)" or an epoxy resin B "FX-305 (manufactured by Nippon Steel Chemical Co., Ltd., epoxy equivalent: 493 g/eq., phosphorus content: 3.0 wt%)" was used as the phosphorus-containing epoxy resin.

Phenol Novolac BRG-557 (PN) (manufactured by Showa Highpolymer Co., Ltd., OH equivalent: 105, softening point: 86°C) or dicyandiamide (DICY) (manufactured by NIPPON CARBIDE INDUSTRIES CO., INC.) was used as the curing agent.

2-Ethyl-4-methylimidazole (2E4MZ) (manufactured by SHIKOKU CHEMICALS CORPORATION) was used as the curing accelerator.

A mixed solvent containing 2-methoxypropanol (manufactured by Tokyo Chemical Industry Co., Ltd.) and methyl ethyl ketone (manufactured by KANTO CHEMICAL CO., INC.) at a ratio of 50/50 was used as the solvent.

A glass cloth (manufactured by Nitto Boseki Co., Ltd., WEA116E106S136, thickness: 0.1 mm) was used as the inorganic filler.

[0060] (1) Measurement of epoxy equivalent

The epoxy equivalent of a resin was measured with a potentiometric titrator as described below. The resin was dissolved in methyl ethyl ketone as a solvent, a solution of tetraethylammonium bromide in acetic acid was added to the solution, it was titrated with a 0.1 mol/L solution of perchloric acid in acetic acid in the potentiometric titrator.

[0061] (2) Coefficient of linear expansion (CTE) and glass transition point (T_g)

The T_g of the cured product was determined with a TMA120C-type thermomechanical measuring apparatus manufactured by Seiko Instruments Inc. under a condition of a rate of temperature increase of 10°C/min, its α_1 (CTE at temperatures lower than the T_g) was determined from an average in the range of from 30 to 50°C, and its α_2 (CTE at temperatures higher than the T_g) was determined from an average in the range of from $T_g+20^\circ\text{C}$ to $T_g+40^\circ\text{C}$.

[0062] (3) Water absorption coefficient

The conditions of a temperature of 25°C and a relative humidity of 50% were defined as a normal state, and a weight change ratio

after the cured product had been caused to absorb moisture under the conditions of a temperature of 85°C and a relative humidity of 85% for 100 hr was defined as its water absorption coefficient.

[0063] (4) Dielectric constant and dielectric loss tangent

Evaluations were performed through the determination of the dielectric constant and dielectric loss tangent of the cured product at a frequency of 2.1 GHz with an ADMS010c-type dielectric constant-measuring apparatus manufactured by AET, INC. by a coaxial resonator method.

[0064] (5) Flame retardancy

A test piece having a thickness of 0.5 mm was produced and evaluated by the UL94V-0 standard, and the flame retardancy of the cured product was represented by the total combustion time of five test pieces.

[0065] Table 1

	Example 1	Example 2	Example 3	Example 4
StPNE-A	50.0	50.0	50.0	50.0
Epoxy resin A	50.0		50.0	
Epoxy resin B		50.0		50.0
PN	36.3	30.1		
DICY			3.6	3.0
2E4MZ	0.1	0.5	0.1	0.5
Solvent	136.3	130.1	103.6	103.0

[0066] Table 2

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
StPNE-A	100.0			
Epoxy resin A		100.0		
Epoxy resin B			100.0	100.0
PN	38.9	33.8	21.3	
DICY				2.1
2E4MZ	0.1	0.1	0.5	0.5
Solvent	138.9	133.8	121.3	102.1

[0067] Table 3

	Example 1	Example 2	Example 3	Example 4
Tg (°C)	137	110	132	112
CTE (α_1 , <Tg)	35	30	33	29
CTE (α_2 , >Tg)	250	276	252	261
Water absorption coefficient (wt%)	0.60	0.68	0.65	0.69
Dielectric constant (2.1 GHz)	3.43	3.44	3.47	3.48
Dielectric loss tangent (2.1 GHz)	0.013	0.014	0.015	0.015
Combustion time (sec)	85	81	78	72

[0068] Table 4

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Tg (°C)	130	148	112	106
CTE (ppm, <Tg)	28	43	44	36
CTE (ppm, >Tg)	243	276	378	255
Water absorption coefficient (wt%)	0.50	0.82	0.91	1.02
Dielectric constant (2.1 GHz)	3.42	3.77	3.80	3.82
Dielectric loss tangent (2.1 GHz)	0.012	0.029	0.030	0.033
Combustion time (sec)	131	72	60	35

Industrial Applicability

[0069] The epoxy resin composition of the present invention provides a cured product excellent in low dielectric property and flame retardancy, and can be suitably used in an application such as the sealing of electrical and electronic parts, or a printed wiring board material. In particular, the composition is excellent in low dielectric property and flame retardancy, and eliminates the need for, or reduces, the use of a flame retardant that has an environmental load while expressing an excellent low dielectric constant and excellent low dielectric loss tangent as a printed wiring board for a high-frequency band.

Claims

[Claim 1] An epoxy resin composition, comprising:

epoxy resins;

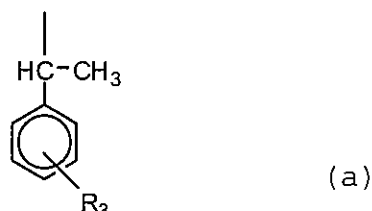
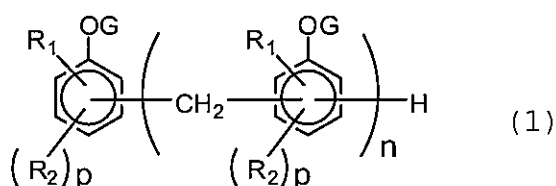
a curing agent; and

an inorganic filler,

wherein:

the epoxy resins comprise, as epoxy resin components, an epoxy resin represented by the following general formula (1) and a phosphorus-containing epoxy resin having a phosphorus content of from 1.0 to 5.0 wt%; and

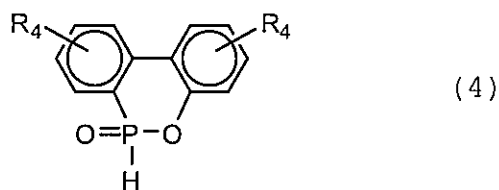
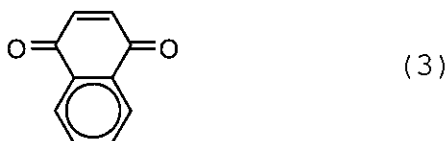
a content of the epoxy resin represented by the general formula (1) is 30 wt% or more and a content of the phosphorus-containing epoxy resin is 30 wt% or more with respect to an entirety of the epoxy resins:



wherein, G represents a glycidyl group, R₁ represents hydrogen or a hydrocarbon group having 1 to 6 carbon atoms, R₂ represents a substituent represented by the formula (a), n represents a number of from 1 to 20, p represents a number of from 0.1 to 2.5, and R₃

represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms.

[Claim 2] An epoxy resin composition according to claim 1, wherein the phosphorus-containing epoxy resin comprises a phosphorus-containing epoxy resin obtained by causing an epoxy resin having two or more epoxy groups per molecule, a quinone compound represented by the following formula (2) or (3), and a phosphorus compound having one active hydrogen bonded to a phosphorus atom represented by the following formula (4) to react with one another:



wherein, R₄ represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms.

[Claim 3] An epoxy resin composition according to claim 1, wherein the inorganic filler comprises a fibrous glass base material.

[Claim 4] An epoxy resin cured product, which is obtained by curing

the epoxy resin composition according to any one of claims 1 to 3.