DESCRIPTION

TITLE OF INVENTION:

CURABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF

Technical Field

[0001] The invention relates to a curable resin composition including a compound having a specific structure and a cured product thereof, and is suitably used for electrical and electronic components, such as a semiconductor encapsulant, a printed wiring board, and a build-up laminate, a lightweight high-strength material such as carbon fiber reinforced plastics and glass fiber reinforced plastics, and 3D printing applications.

Related Art

[0002] In recent years, regarding laminates on which electrical and electronic components are mounted, the required properties have become widened and advanced due to the expansion of the fields of application. While conventional semiconductor chips are mainly mounted on metal lead frames, it has become more and more common to mount semiconductor chips with high processing capabilities, such as central processing units (hereinafter referred to as CPUs), on laminates made of polymer materials.

[0003] In the fifth-generation ("5G") communication system whose development is currently accelerating, further progresses in high capacity and high-speed communication are expected. With 5G, the frequencies used are higher. However, to realize high-speed communication using high frequencies, it is important to suppress transmission loss, and further reduction of the dielectric loss tangent of substrate materials is demanded. Transmission loss that occurs on printed circuit boards is due to conductor loss and dielectric loss. As described in Non-Patent Document 1, the conductor loss is proportional to the square root of the dielectric constant of the dielectric body and the dielectric loss tangent. Therefore, it can be said that improving the

dielectric loss tangent, which has a greater contribution than the dielectric constant, is effective in terms of transmission loss reduction. As low dielectric materials, examples include thermoplastic materials represented by polytetrafluoroethylene (PTFE) and liquid crystal polymer (LCP). However, thermoplastic materials have poorer moldability than thermosetting resins. Based on the above, the development of thermosetting resins and curable resin compositions that exhibit a low dielectric loss tangent is desired.

[0004] With such background, thermosetting resin compositions that exhibit a low dielectric loss tangent are being studied. For example, Patent Document 1 discloses a curable resin composition including bisvinylphenylethane (BVPE) and thermosetting polyphenylene ether (Patent Document 1). In the curable resin composition, the storage stability of the resin composition is improved by using a polymerization inhibitor, and 2,5-bis(1,1-dimethylbutyl)hydroquinone is used. In general, in the case where a polymerization inhibitor having a polar group (a substituent having a hetero-atom) in its structure is used, the storage stability improves as the addition amount increases. However, the dielectric properties deteriorate in a trade-off relationship, and the optimal polymerization inhibitor varies with the target compound for which storage stability is to be improved, so the selection is difficult and considered an important issue.

[Prior Art Document(s)]

[Non-patent Document(s)]

[0005] Signal Loss Factors in High-Speed Signal Transmission on Printed Circuit Boards (Mitsui Mining & Smelting Co., Ltd.) 29th Japan Institute of Electronics Packaging Spring Conference 16, P1-17

[Patent Document(s)]

[0006] [Patent Document 1] Japanese Patent Application Laid-open No. 2008-115280

SUMMARY OF INVENTION

[Issues to be solved by the invention]

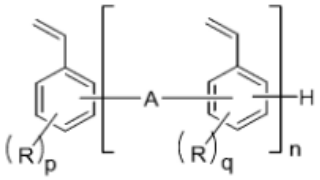
[0007] The invention has been made in view of such circumstances, and aims to provide a curable resin composition that exhibits excellent storage stability and low dielectric loss tangent, and a cured product thereof.

[Means for solving the issues]

[0008] That is, the invention relates [1] to [5] in the following. In the application, "(numerical value 1) to (numerical value 2)" indicates that the upper and lower limit values are included.

[1] A curable resin composition includes: a compound represented by formula (1) and a compound represented by formula (2).

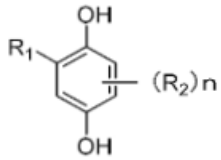
[0009] [Formula 1]



(1)

[0010] (In Formula (1-1), A represents a hydrocarbon group having 1 to 20 carbon atoms, and each of a plurality of R independently represents a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms, and p represents an integer of 0 to 4, q represents an integer of 0 to 3, and n represents an average value for a number of repetitions, which is $1 \leq n \leq 20$.)

[0011] [Formula 2]

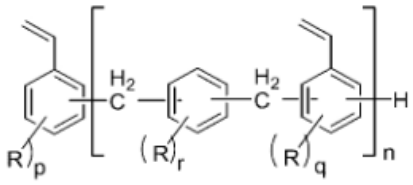


(2)

[0012] (In Formula (2), each of R_1 and R_2 independently represents a hydrocarbon group having 1 to 20 carbon atoms, and n represents an integer of 0 to 3.)

[2] A curable resin composition includes: a compound represented by Formula (1-1) and a compound represented by Formula (2),

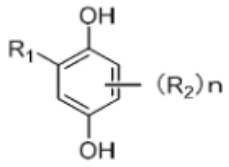
[0013] [Formula 3]



(1-1)

(In Formula (1), each of a plurality of R independently represents a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms, p and r represent integers of 0 to 4, q represents an integer of 0 to 3, and n represents an average value for a number of repetitions, which is $1 \leq n \leq 20$.)

[0014] [Formula 4]



(2)

[0015] (In Formula (2), each of R_1 and R_2 independently represents a hydrocarbon group having 1 to 20 carbon atoms, and n represents an integer of 0 to 3.)

[3] The curable resin composition according to [1] or [2] further includes: a polymerization initiator.

[4] The curable resin composition according to any one of [1] to [3], further includes: at least one selected from a group consisting of a maleimide compound, a polyphenylene ether compound, a compound having an ethylenic unsaturated bond, a cyanate ester resin, polybutadiene and a modified product of polybutadiene, polystyrene and a modified product of polystyrene, polyethylene and a modified product of polyethylene.

[5] A cured product is obtained by curing the curable resin composition according to any one of [1] to [4].

[Inventive effects]

[0016] The curable resin composition of the invention and the cured product thereof exhibit a low dielectric loss tangent.

BRIEF DESCRIPTION OF DRAWINGS

[0017]

[FIG. 1] FIG. 1 illustrates a GPC chart of Synthesis Example 1.

[FIG. 2] FIG. 2 illustrates a GPC chart of Synthesis Example 2.

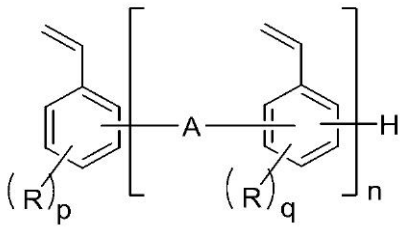
[FIG. 3] FIG. 3 illustrates a ^{1}H-NMR of Synthesis Example 2.

DESCRIPTION OF EMBODIMENTS

[0018] Hereinafter, embodiments according to the invention (hereinafter also referred to as "the embodiments") will be described in further detail.

[0019] The curable resin composition of the embodiment contains a compound represented by formula (1) as follows as an essential component.

[0020] [Formula 5]



(1)

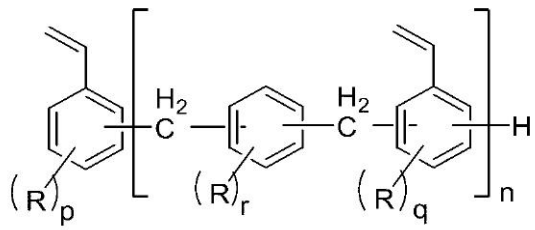
[0021] In formula (1), A is a hydrocarbon group having 1 to 20 carbon atoms, preferably a hydrocarbon group having 2 to 20 carbon atoms, more preferably a hydrocarbon group having 6 to 20 carbon atoms, and particularly preferably a hydrocarbon group having 8 to 20 carbon atoms. The hydrocarbon preferably contains a methylene chain, an alicyclic structure, or an aromatic ring, more preferably contains a methylene chain or an aromatic ring, and even more preferably contains at least one or more aromatic rings. By containing an aromatic ring, molecular vibration

can be suppressed and dielectric properties become favorable. In addition, heat resistance is improved. Multiple Rs each independently represent a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms, preferably a hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms, and more preferably a hydrogen atom or a hydrocarbon group having 1 to 3 carbon atoms. Hydrocarbons having 10 or fewer carbon atoms are less likely to undergo molecular vibration when being exposed to a high frequency, and therefore are particularly excellent in electrical properties.

[0022] In formula (1), p is an integer of 0 to 4, preferably an integer of 0 to 2. q is an integer of 0 to 3, preferably an integer of 0 to 2. n is an average value of the number of repetitions, preferably $1 \leqq n \leqq 20$, more preferably $1.1 \leqq n \leqq 20$, particularly preferably $1.1 \leqq n \leqq 10$, and most preferably $1.1 \leqq n \leqq 5$. The value of n can be calculated from the value of the number average molecular weight (Mn) obtained by gel permeation chromatography (GPC) measurement of the compound represented by formula (1). The number average molecular weight is preferably 200 or more and less than 5000, more preferably 300 or more and less than 3000, and particularly preferably 400 or more and less than 2000. If the weight average molecular weight is less than 5000, purification by water washing becomes easy, and if the weight average molecular weight is 200 or more, the target compound does not volatilize in the solvent distillation step.

[0023] The compound represented by formula (1) is particularly preferably a compound represented by formula (1-1) as follows.

[0024] [Formula 6]



(1-1)

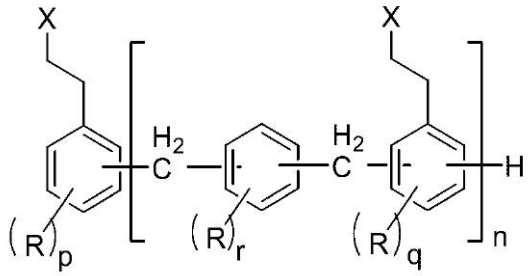
[0025] In formula (1-1), multiple Rs each independently represent a hydrogen atom, a

hydrocarbon group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms, preferably a hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms, and more preferably a hydrogen atom or a hydrocarbon group having 1 to 3 carbon atoms. Hydrocarbons having 10 or fewer carbon atoms are less likely to undergo molecular vibration when being exposed to a high frequency, and therefore are particularly excellent in electrical properties.

[0026] In formula (1-1), p and r are integers of 0 to 4, preferably integers of 0 to 2. q is an integer of 0 to 3, preferably an integer of 0 to 2. n is an average value of the number of repetitions, preferably $1 \leqq n \leqq 20$, more preferably $1.1 \leqq n \leqq 20$, particularly preferably $1.1 \leqq n \leqq 10$, and most preferably $1.1 \leqq n \leqq 5$. The value of n can be calculated from the value of the number average molecular weight (Mn) obtained by gel permeation chromatography (GPC) measurement of the compound represented by formula (1-1). The number average molecular weight is preferably 200 or more and less than 5000, more preferably 300 or more and less than 3000, and particularly preferably 400 or more and less than 2000. If the weight average molecular weight is less than 5000, purification by water washing becomes easy, and if the weight average molecular weight is less than is 200 or more, the target compound does not volatilize in the solvent distillation step.

[0027] The compound represented by formula (1-1) is derived from a compound represented by formula (1-2) as follows.

[0028] [Formula 7]



(1-2)

[0029] In formula (1-2), the definition of R, the values of p, r, q, and n, and the preferred ranges

thereof are the same as those in formula (1-1). X represents a halogen atom, and from the viewpoint of the reactivity and the stability of raw materials, a bromine atom or a chlorine atom is preferred, and a bromine atom is particularly preferred.

[0030] The compound represented by formula (1-1) can be obtained, for example, by a method of subjecting the compound represented by formula (1-2) to a dehydrohalogenation reaction in a solvent in the presence of a basic catalyst. Examples of the solvent to be used include water-insoluble solvents, like aromatic solvents such as toluene and xylene, aliphatic solvents such as cyclohexane and n-hexane, ethers such as diethyl ether and diisopropyl ether, ester solvents such as ethyl acetate and butyl acetate, and ketone solvents such as methyl isobutyl ketone and cyclopentanone. However, the solvents are not limited to these solvents, and two or more types may be used in combination. In addition to the water-insoluble solvents, aprotic polar solvents can also be used in combination. Examples include dimethyl sulfone, dimethyl sulfoxide, dimethylformamide, dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, and N-methylpyrrolidone, and two or more types may be used in combination. In the case where an aprotic polar solvent is used, it is preferred to use an aprotic polar solvent having a higher boiling point than the water-insoluble solvent used in combination. The catalyst is not particularly limited, but examples include basic catalysts such as sodium hydroxide, potassium hydroxide, and potassium carbonate. Since it is difficult to completely proceed with the dehydrohalogenation reaction, the aprotic polar solvent may be used in large excess relative to the substrate, or the dehydrohalogenation reaction may be repeated multiple times, such as two or three or more times. For example, after performing the dehydrohalogenation reaction of the compound represented by formula (1-2) in an organic solvent in the presence of a basic catalyst and washing the obtained solution with water, the solution may be returned to the reaction vessel again, and a basic catalyst may be added to perform the reaction again. By doing so, the progress of the dehydrohalogenation reaction can be enhanced. That is, it is possible to reduce the amount of

residual halogen contained in the target compound. The residual halogen amount is preferably 1 ppm to 10,000 ppm in the target product, more preferably 1 ppm to 1,000 ppm, and even more preferably 1 ppm to 750 ppm. In the case of a large amount of residual halogen contained in the compound represented by formula (1-1), molecular vibration occurs at the time of being exposed to high frequency, which adversely affects electrical properties, such as dielectric loss tangent in particular. Moreover, in the case of a large amount of residual halogen, the risk of causing problems such as metal corrosion, ion migration, etc., increases in environmental tests such as high accelerated stress test (HAST), so the above halogen content is preferred.

[0031] The production method of the compound represented by formula (1-2) is not particularly limited, but, for example, a compound having a (2-bromoethyl)benzene structure and a bishalogenated methylaryl compound (or a bishydroxymethylaryl compound, etc.,) may be reacted under an acid catalyst such as hydrochloric acid, sulfonic acid, or activated clay, or a compound having a (2-bromoethyl)benzene structure and a bishydroxymethylaryl compound may be reacted under an acid catalyst such as hydrochloric acid, sulfonic acid, or activated clay. In the case where sulfonic acid, etc., is used as a catalyst, the neutralization with an alkali metal such as sodium hydroxide or potassium hydroxide may be performed before proceeding to an extraction step. For the extraction step, an aromatic hydrocarbon solvent such as toluene or xylene may be used alone, or an non-aromatic hydrocarbon such as cyclohexane or toluene may be used in combination. After extraction, the organic layer is washed with water until the wastewater becomes neutral, and the solvent and excess compound having a (2-bromoethyl)benzene structure are distilled off by using an evaporator, etc., to obtain a compound having at least two or more (2-bromoethyl)benzene structures in the target molecule.

[0032] Examples of the compound having a (2-bromoethyl)benzene structure include (2-bromoethyl)benzene, 1-(2-bromoethyl)-2-methylbenzene, 1-(2-bromoethyl)-3-methylbenzene, 1-(2-bromoethyl)-4-methylbenzene, 1-(2-bromoethyl)-2,3-dimethylbenzene, 1-(2-bromoethyl)-2,4-

dimethylbenzene, 1-(2-bromoethyl)-2,5-dimethylbenzene, 1-(2-bromoethyl)-2,6-dimethylbenzene, etc. However, the invention is not limited thereto. The above may be used alone or in combination of two or more. Although solvent solubility improves with a higher carbon number, heat resistance decreases, so it is preferable to be unsubstituted or substituted with an alkyl group having 1 to 3 carbon atoms, more preferable to be unsubstituted or substituted with an alkyl group having 1 to 2 carbon atoms, and most preferable to be unsubstituted or substituted with a methyl group.

[0033] Examples of the bishalogenated methylaryl compound include o-xylylene difluoride, m-xylylene difluoride, p-xylylene difluoride, o-xylylene dichloride, m-xylylene dichloride, p-xylylene dichloride, o-xylylene dibromide, m-xylylene dibromide, p-xylylene dibromide, o-xylylene diiodide, m-xylylene diiodide, p-xylylene diiodide, etc. However, the invention is not limited thereto. The above may be used alone or in combination of two or more. From the viewpoint of reactivity of raw materials during synthesis, chloride-based compounds, bromide-based compounds, and iodide-based compounds are preferable, and more preferably chloride-based compounds and bromide-based compounds are listed.

[0034] Examples of bishydroxymethylaryl compounds include o-benzenedimethanol, m-benzenedimethanol, p-benzenedimethanol, etc. However, the invention is not limited thereto. The above may be used alone or in combination of two or more. The usage amount of the above is preferably 0.05 to 0.8 parts by mass, and more preferably 0.1 to 0.6 parts by mass, relative to 1 part by mass of the compound having a (2-bromoethyl)benzene structure.

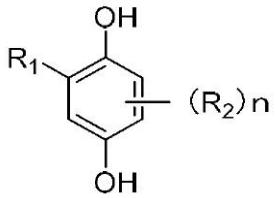
[0035] At the time of the reaction between the compound having a (2-bromoethyl)benzene structure and the halogenated methylaryl compounds, a catalyst, such as hydrochloric acid, phosphoric acid, sulfuric acid, formic acid, p-toluenesulfonic acid, methanesulfonic acid, as well as Lewis acids such as aluminum chloride and zinc chloride, solid acids such as activated clay, acid clay, white carbon, zeolite, and silica alumina, and acidic ion exchange resins can be used as

necessary. The above may be used alone or in combination of two or more. The usage amount of the catalyst is 0.05 mol to 0.8 mol, preferably 0.1 mol to 0.7 mol, relative to 1 mol of the compound having a (2-bromoethyl)benzene structure that is used. In the case where the catalyst usage amount is excessively large, the viscosity of the reaction solution may become too high, making stirring difficult, and in the case where the catalyst usage amount is excessively small, the progress of the reaction may become slow. The reaction may be performed by selecting and using an organic solvent such as hexane, cyclohexane, octane, toluene, xylene as necessary, or may be performed without a solvent. For example, after adding an acidic catalyst to a mixed solution of the compound having a (2-bromoethyl)benzene structure, the halogenated methylaryl compound, and the solvent, in the case where the catalyst contains water, water is removed from the system by azeotropic distillation. Thereafter, the reaction is performed at 40°C to 180°C, preferably 50°C to 170°C for 0.5 hours to 20 hours. After completion of the reaction, the acidic catalyst may be neutralized with an alkaline aqueous solution, but it is also possible to proceed to a water washing process without neutralization. Regarding the water washing process, a water-insoluble organic solvent is added to the oil layer and water washing is repeated until the wastewater becomes neutral.

[0036] The softening point of the compound represented by the formula (1-2) is preferably 80°C or lower, more preferably 70°C or lower. In the case where the softening point is 80°C or lower, the viscosity decreases at the time of induction to the compound represented by the formula (1-1). Accordingly, it becomes easy to secure fluidity, the impregnation properties into glass cloth, carbon fiber, etc., are not impaired, and B-staging such as prepreg formation becomes easy. In the case where the viscosity decreases by increasing a diluting solvent, there is a possibility that the resin does not sufficiently adhere to the fibrous material in the impregnation process.

[0037] The curable resin composition of the embodiment contains a compound represented by formula (2) as follows.

[0038] [Formula 8]



(2)

[0039] In formula (2), R_1 and R_2 each independently represent a hydrocarbon group having 1 to 20 carbon atoms, preferably a hydrocarbon group having 1 to 15 carbon atoms, more preferably a hydrocarbon group having 1 to 10 carbon atoms, and even more preferably a hydrocarbon group having 1 to 5 carbon atoms. In the case where R_1 and R_2 are hydrocarbon groups having more than 20 carbon atoms, molecular vibration tends to occur at the time of exposure to high frequency, and there is a risk that dielectric properties may deteriorate. When the number of carbon atoms is 20 or less, the equivalent per unit weight of the phenolic hydroxyl group increases, and a sufficient polymerization inhibition effect can be obtained. n is an integer of 0 to 3, preferably 0 to 2, more preferably 0 to 1, and particularly preferably 0. In the case where n is small, the equivalent per unit weight of the phenolic hydroxyl group becomes large, and a sufficient polymerization inhibition effect can be obtained, so it can be said to be more preferable.

[0040] The compound represented by formula (2) has a hydrocarbon group at the ortho position and a phenolic hydroxyl group at the para position relative to the phenolic hydroxyl group located on the upper side of formula (2). The hydrocarbon group has an effect of enhancing the polymerization inhibition effect since hydrogen is supplied to the phenoxy radical to regenerate a phenolic hydroxyl group. The phenolic hydroxyl group at the para position has an effect of improving radical scavenging performance since the electron density of the compound represented by formula (2) is increased. Moreover, since polar groups are positioned symmetrically in the compound represented by formula (2), the dipole moment is small and the deterioration of dielectric properties can be suppressed.

[0041] The compound represented by formula (2) is preferably 0.0001 parts by mass to 1 part

by mass, more preferably 0.001 parts by mass to 0.75 parts by mass, even more preferably 0.002 parts by mass to 0.5 parts by mass, and particularly preferably 0.004 parts by mass to 0.5 parts by mass, relative to 100 parts by mass of the compound represented by formula (1). In the case where the compound is less than 0.0001 parts by mass, there is a risk that a sufficient polymerization inhibition effect cannot be obtained, and in the case where the compound is more than 1 part by mass, there is a risk that dielectric properties may be significantly impaired.

[0042] In the case where the curable resin composition of the embodiment is used for prepreg application, since the general drying temperature of prepreg is at most 120°C, the reaction initiation temperature of the curable resin composition is preferably 120°C or higher. However, since the reaction initiation temperature obtained by DSC is a non-adiabatic system and differs from the actual temperature (see: Explosion Safety Information Database for Chemical Substances, http://www.explosion-safety.jp/INFOMATION/how_to_test_1-3.htm), the exothermic initiation temperature by DSC preferably becomes at least 170°C or higher. In the case of less than 170°C, the reaction proceeds during drying of the prepreg, resulting in no fluidity during molding, and there is a risk that creation of a laminated plate becomes difficult.

[0043] The curable resin composition of the embodiment can also improve the performance by adding various materials in addition to the compound represented by formula (1) and the compound represented by formula (2).

[0044] [Polymerization inhibitor]

The curable resin composition of the embodiment may contain other polymerization inhibitors in addition to the compound represented by formula (2). However, in the case where a polymerization inhibitor is used, the addition amount is limited to a range that does not significantly affect the dielectric properties and the curing properties of the curable resin composition of the embodiment.

[0045] Examples of the polymerization inhibitor include phenol-based, sulfur-based,

phosphorus-based, hindered amine-based, nitroso-based, nitroxyl radical-based polymerization inhibitor, etc.

[0046] Examples of the phenol-based polymerization inhibitor include monophenols such as 2,6-di-t-butyl-p-cresol, butylated hydroxyanisole, 2,6-di-t-butyl-p-ethylphenol, stearyl-β-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, isooctyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-t-butylanilino)-1,3,5-triazine, 2,4-bis[(octylthio)methyl]-o-cresol; bisphenols such as 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-hydrocinnamide), 2,2-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,5-di-t-butyl-4-hydroxybenzylphosphonate-diethyl ester, 3,9-bis[1,1-dimethyl-2-{β-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]2,4,8,10-tetraoxaspiro[5,5]undecane, calcium bis(3,5-di-t-butyl-4-hydroxybenzylsulfonate); and polymeric phenols such as 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, bis[3,3'-bis-(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, tris-(3,5-di-t-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)-s-triazine-2,4,6-(1H,3H,5H)trione, tocopherol. However, the invention is not limited thereto.

[0047] Examples of the sulfur-based polymerization inhibitor include dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate. However, the invention is not limited thereto.

[0048] Examples of the phosphorus-based polymerization inhibitor include phosphites such as triphenyl phosphite, diphenyl isodecyl phosphite, phenyl diisodecyl phosphite, tris(nonylphenyl)

phosphite, diisodecyl pentaerythritol phosphite, tris(2,4-di-t-butylphenyl) phosphite, cyclic neopentanetetrayl bis(octadecyl) phosphite, cyclic neopentanetetrayl bis(2,4-di-t-butylphenyl) phosphite, cyclic neopentanetetrayl bis(2,6-di-t-butyl-4-methylphenyl) phosphite, bis[2-t-butyl-6-methyl-4-{2-(octadecyloxycarbonyl)ethyl}phenyl] hydrogen phosphite; oxaphosphaphenanthrene oxides such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-(3,5-di-t-butyl-4-hydroxybenzyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-decyloxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. However, the invention is not limited thereto.

[0049] Examples of the hindered amine-based polymerization inhibitor include ADEKA STAB LA-40MP, ADEKA STAB LA-40Si, ADEKA STAB LA-402AF, ADEKA STAB LA-87, ADEKA STAB LA-82, ADEKA STAB LA-81, ADEKA STAB LA-77Y, ADEKA STAB LA-77G, ADEKA STAB LA-72, ADEKA STAB LA-68, ADEKA STAB LA-63P, ADEKA STAB LA-57, ADEKA STAB LA-52, Chimassorb2020FDL, Chimassorb944FDL, Chimassorb944LD, Tinuvin622SF, TinuvinPA144, Tinuvin765, Tinuvin770DF, TinuvinXT55FB, Tinuvin111FDL, Tinuvin783FDL, Tinuvin791FB. However, the invention is not limited thereto.

[0050] Examples of the nitroso-based polymerization inhibitor include p-nitrosophenol, N-nitrosodiphenylamine, ammonium salt of N-nitrosophenylhydroxyamine (cupferron). However, the invention is not limited thereto. Among these, the ammonium salt of N-nitrosophenylhydroxyamine (cupferron) is preferred.

[0051] Examples of the nitroxyl radical-based polymerization inhibitor include di-tert-butyl nitroxide, 2,2,6,6-tetramethylpiperidine-1-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-acetoxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl. However, the invention is not limited thereto.

[0052] [Curing accelerator]

The curability of the curable resin composition of the embodiment can also be improved by adding a curing accelerator. As the curing accelerator, an anionic curing accelerator that promotes curing reaction by generating anions through irradiation with ultraviolet light or visible light or heating, or a cationic curing accelerator that promotes a curing reaction by generating cations through irradiation with ultraviolet light or visible light or heating is preferred.

[0053] Examples of the anionic curing accelerator include imidazoles such as 2-methylimidazole, 2-ethylimidazole, and 2-ethyl-4-methylimidazole; trialkylamines such as triethylamine and tributylamine; 4-dimethylaminopyridine, benzyldimethylamine, 2,4,6-tris(dimethylaminomethyl)phenol, 1,8-diazabicyclo(5,4,0)-undecene, with 4-dimethylaminopyridine and 1,8-diazabicyclo(5,4,0)-undecene being preferred. Other examples include phosphines such as triphenylphosphine; quaternary ammonium salts such as tetrabutylammonium salt, triisopropylmethylammonium salt, trimethyldecanylammonium salt, cetyltrimethylammonium salt, and hexadecyltrimethylammonium hydroxide. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0054] Examples of the cationic curing accelerator include quaternary phosphonium salts such as triphenylbenzylphosphonium salt, triphenylethylphosphonium salt, and tetrabutylphosphonium salt (the counter ions of the quaternary salts are not particularly specified, such as halogen, organic acid ions, hydroxide ions, etc., but organic acid ions and hydroxide ions are particularly preferred); transition metal compounds (transition metal salts) such as tin octylate, zinc carboxylates (zinc 2-ethylhexanoate, zinc stearate, zinc behenate, zinc myristate), and zinc phosphate esters (zinc octyl phosphate, zinc stearyl phosphate). However, the invention is are not limited thereto. The above may be used alone or in combination of multiple types.

[0055] The blending amount of the curing accelerator is 0.01 parts by mass to 5.0 parts by mass

per 100 parts by mass of the curable resin composition, used as necessary.

[0056] [Inorganic filler]

The curable resin composition of the embodiment may contain an inorganic filler. Examples of the inorganic filler include powders such as fused silica, crystalline silica, porous silica, alumina, zircon, calcium silicate, calcium carbonate, quartz powder, silicon carbide, silicon nitride, boron nitride, zirconia, aluminum nitride, graphite, forsterite, steatite, spinel, mullite, titania, talc, clay, iron oxide, asbestos, and glass powder, or inorganic fillers obtained by forming the fillers into spherical or crushed shapes. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0057] The usage amount of the inorganic filler in the case of obtaining a curable resin composition for semiconductor encapsulation is preferably 80 to 92 parts by mass, and more preferably 83 parts by mass to 90 parts by mass, per 100 parts by mass of the curable resin composition. In the case of obtaining a curable resin composition for a substrate material such as an interlayer insulating layer forming material, a copper-clad laminate, a prepreg, RCC, etc., the usage amount of the inorganic filler is preferably 5 parts by mass to 80 parts by mass, and more preferably 10 parts by mass to 60 parts by mass, per 100 parts by mass of the curable resin composition.

[0058] [Polymerization initiator]

The curability of the curable resin composition of the embodiment can be improved by adding a polymerization initiator. A polymerization initiator is a compound capable of polymerizing an olefin functional group such as an ethylenic unsaturated bond, and examples include olefin metathesis polymerization initiators, anionic polymerization initiators, cationic polymerization initiators, and radical polymerization initiators. Among the above, it is preferable to use a radical polymerization initiator that possesses curability and appropriate stability. A radical polymerization initiator refers to a compound that generates radicals upon irradiation with

ultraviolet light or visible light or upon heating, and initiates a chain polymerization reaction. Examples of the radical polymerization initiator that can be used include organic peroxides, azo compounds, and benzopinacols, with organic peroxides being preferred for exhibiting less influence on curing temperature control, outgas suppression, and electrical properties of decomposition products.

[0059] Examples of the organic peroxides include ketone peroxides such as methyl ethyl ketone peroxide and acetylacetone peroxide; diacyl peroxides such as benzoyl peroxide; dialkyl peroxides such as dicumyl peroxide and 1,3-bis-(t-butylperoxyisopropyl)benzene; peroxyketals such as t-butylperoxybenzoate and 1,1-di-t-butylperoxycyclohexane; alkyl peresters such as α-cumylperoxyneodecanoate, t-butylperoxyneodecanoate, t-butylperoxypivalate, 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate, t-amylperoxy-2-ethylhexanoate, t-butylperoxy-2-ethylhexanoate, t-amylperoxy-3,5,5-trimethylhexanoate, t-butylperoxy-3,5,5-trimethylhexanoate, and t-amylperoxybenzoate; peroxycarbonates such as di-2-ethylhexylperoxydicarbonate, bis(4-t-butylcyclohexyl)peroxydicarbonate, t-butylperoxyisopropylcarbonate, and 1,6-bis(t-butylperoxycarbonyloxy)hexane; t-butyl hydroperoxide, cumene hydroperoxide, t-butylperoxyoctoate, and lauroyl peroxide. However, the invention is not limited therto. The above may be used alone or in combination of multiple types. Among the organic peroxides, ketone peroxides, diacyl peroxides, hydroperoxides, dialkyl peroxides, peroxyketals, alkyl peresters, and peroxycarbonates are preferable, and dialkyl peroxides are more preferable.

[0060] Examples of the azo compounds include azobisisobutyronitrile, 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis(2,4-dimethylvaleronitrile), and the like. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0061] The addition amount of the polymerization initiator is preferably 0.01 parts by mass to 5 parts by mass, and particularly preferably 0.01 parts by mass to 3 parts by mass, per 100 parts by mass of the curable resin composition. In the case where the amount of the polymerization

initiator that is used is less than 0.01 parts by mass, the molecular weight may not be sufficiently extended during the polymerization reaction, and in the case where the amount of the polymerization initiator that is used is more than 5 parts by mass, dielectric properties such as dielectric constant and dielectric loss tangent may be impaired.

[0062] [Flame retardant]

The curable resin composition of the embodiment may use a flame retardant. Examples of the flame retardant include halogen-based flame retardants, inorganic flame retardants (antimony compounds, metal hydroxides, nitrogen compounds, boron compounds, etc.), phosphorus-based flame retardants, etc. However, phosphorus-based flame retardants are preferable from the viewpoint of achieving halogen-free flame retardancy.

The phosphorus-based flame retardant may be either a reactive type or an additive type. Specific examples include, in addition to, phosphoric acid esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylene phosphate, cresyl diphenyl phosphate, cresyl-2,6-dixylene phosphate, 1,3-phenylene bis(dixylene phosphate), 1,4-phenylene bis(dixylene phosphate), and 4,4'-biphenyl(dixylene phosphate); and phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10-(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide, phosphorus-containing epoxy compounds obtained by reacting epoxy resin with active hydrogen of the phosphanes; red phosphorus; and the like. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types. Among the above exemplified substances, phosphoric acid esters, phosphanes, or phosphorus-containing epoxy compounds are preferable, and 1,3-phenylene bis(dixylene phosphate), 1,4-phenylene bis(dixylene phosphate), 4,4'-biphenyl(dixylene phosphate), or phosphorus-containing epoxy compounds are particularly preferable.

[0063] The content of the flame retardant is preferably in the range of 0.1 parts by mass to 0.6 parts by mass per 100 parts by mass of the curable resin composition. In the case where the

content of the flame retardant is less than 0.1 parts by mass, flame retardancy may be insufficient, and in the case where the content of the flame retardant is more than 0.6 parts by mass, the hygroscopicity and dielectric properties of the cured product may be adversely affected.

[0064] [Light stabilizer]

The curable resin composition of the embodiment may use a light stabilizer. As the light stabilizer, hindered amine-based light stabilizers, particularly HALS and the like, are suitable. Examples of HALS include dibutylamine·1,3,5-triazine·N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl-1,6-hexamethylenediamine and the reaction product of N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, the reaction product of dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine, poly[{6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)imino}hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}], bis(1,2,2,6,6-pentamethyl-4-piperidyl)[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, 2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonic acid bis(1,2,2,6,6-pentamethyl-4-piperidyl), etc. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0065] The content of the light stabilizer is preferably in the range of 0.001 parts by mass to 0.1 parts by mass per 100 parts by mass of the curable resin composition. In the case where the content of the light stabilizer is less than 0.001 parts by mass, it may be insufficient to exhibit the light stabilizing effect, and in the case where the content of the light stabilizer is more than 0.1 parts by mass, the hygroscopicity and dielectric properties of the cured product may be adversely affected.

[0066] [Binder resin]

The curable resin composition of the embodiment may use a binder resin. Examples of the binder

resin include butyral-based resins, acetal-based resins, acrylic resins, epoxy-nylon-based resins, NBR-phenol resins, epoxy-NBR-based resins, silicone-based resins, and the like. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0067] The blending amount of the binder resin is preferably in a range that does not impair the flame retardancy and heat resistance of the cured product, and is preferably 0.05 to 50 parts by mass per 100 parts by mass of the curable resin composition, and more preferably 0.05 to 20 parts by mass is used as necessary.

[0068] [Additives]

The curable resin composition of the embodiment may use an additive. Examples of the additive include modified products of acrylonitrile copolymers, polyethylene, fluororesins, silicone gels, silicone oils, surface treatment agents for fillers such as silane coupling agents, release agents, carbon black, phthalocyanine blue, coloring agents such as phthalocyanine green, and the like.

[0069] The blending amount of the additive is preferably 1,000 parts by mass or less, more preferably 700 parts by mass or less, per 100 parts by mass of the curable resin composition.

[0070] The curable resin composition of the embodiment may further use epoxy resin, active ester compounds, phenol resin, polyphenylene ether compounds, amine resin, compounds having an ethylenic unsaturated bond, isocyanate resin, polyamide resin, maleimide compound, cyanate ester resin, polyimide resin, polybutadiene and modified products thereof, polystyrene and modified products thereof, polyethylene and modified products thereof, and the like, and the above may be used alone or multiple types may be used in combination. Among the compounds, considering the balance of heat resistance, adhesion, and dielectric properties, it is preferable to contain maleimide compounds, polyphenylene ether compounds, compounds having ethylenic unsaturated bond, cyanate ester resin, polybutadiene and modified products thereof, polystyrene and modified products thereof, polyethylene and modified products thereof. By containing the

compounds, the brittleness of the cured product can be improved and the adhesion to metal can be enhanced, and package cracks in reliability tests such as solder reflow and thermal cycling can be suppressed. The total usage amount of the compounds is, unless otherwise specified, preferably 10 parts by mass or less, more preferably 5 parts by mass or less, particularly preferably 3 parts by mass or less, relative to the mixture of the embodiment. Moreover, the preferable lower limit is 0.1 parts by mass or more, more preferably 0.25 parts by mass or more, still more preferably 0.5 parts by mass or more. Within such range, the effect of each compound to be added can be added while utilizing the low dielectric properties (low dielectric loss tangent) effect of the compound represented by formula (1). For such components, those exemplified below can be used.

[0071] [Epoxy resin]

Preferable epoxy resins are exemplified below. However, the invention is not limited thereto. The properties of the epoxy resin may be liquid or solid, and may be used alone or multiple types may be used in combination.

[0072] Examples of the liquid epoxy resin include bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol AF type epoxy resins, naphthalene type epoxy resins, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, phenol novolac type epoxy resins, alicyclic epoxy resins having an ester skeleton, cyclohexane type epoxy resins, cyclohexane dimethanol type epoxy resins, and epoxy resins having a butadiene structure. Specific examples include "RE310S", "RE410S" (manufactured by Nippon Kayaku Co., Ltd., bisphenol A type epoxy resin), "RE303S", "RE304S", "RE403S", "RE404S" (manufactured by Nippon Kayaku Co., Ltd., bisphenol F type epoxy resin), "HP4032", "HP4032D", "HP4032SS" (manufactured by DIC Corporation, naphthalene type epoxy resin), "828US", "jER828EL", "825", "828EL" (manufactured by Mitsubishi Chemical Corporation, bisphenol A type epoxy resin), "jE807", "1750" (manufactured by Mitsubishi Chemical Corporation, bisphenol F type epoxy resin),

"jER152" (manufactured by Mitsubishi Chemical Corporation, phenol novolac type epoxy resin), "630", "630LSD" (manufactured by Mitsubishi Chemical Corporation, glycidyl amine type epoxy resin), "ZX1059" (manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., mixture of bisphenol A type epoxy resin and bisphenol F type epoxy resin), "EX-721" (manufactured by Nagase ChemteX Corporation, glycidyl ester type epoxy resin), "Celoxide 2021P" (manufactured by Daicel Corporation, alicyclic epoxy resin having an ester skeleton), "PB-3600" (manufactured by Daicel Corporation, epoxy resin having a butadiene structure), "ZX1658", "ZX1658GS" (manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., liquid 1,4-glycidyl cyclohexane type epoxy resin), and the like. The above may be used alone or in combination of two or more types.

[0073] As the solid epoxy resin include bixylenol type epoxy resins, naphthalene type epoxy resins, naphthalene type tetrafunctional epoxy resins, cresol novolac type epoxy resins, dicyclopentadiene type epoxy resins, trisphenol type epoxy resins, naphthol type epoxy resins, biphenyl type epoxy resins, naphthylene ether type epoxy resins, anthracene type epoxy resins, bisphenol A type epoxy resins, bisphenol AF type epoxy resins, and tetraphenylethane type epoxy resin are preferred, and examples may include naphthol type epoxy resins, bisphenol AF type epoxy resins, naphthalene type epoxy resins, and biphenyl type epoxy resins. Specific examples include "HP4032H" (manufactured by DIC Corporation, naphthalene type epoxy resin), "HP-4700", "HP-4710" (manufactured by DIC Corporation, naphthalene type tetrafunctional epoxy resin), "N-690" (manufactured by DIC Corporation, cresol novolac type epoxy resin), "N-695" (manufactured by DIC Corporation, cresol novolac type epoxy resin), "HP-7200", "HP-7200HH", "HP-7200H" (manufactured by DIC Corporation, dicyclopentadiene type epoxy resin), "EXA-7311", "EXA-7311-G3", "EXA-7311-G4", "EXA-7311-G4S", "HP-6000" (manufactured by DIC Corporation, naphthylene ether type epoxy resin), "EPPN-502H" (manufactured by Nippon Kayaku Co., Ltd., trisphenol type epoxy resin), "NC-7000L", "NC-7300" (manufactured by

Nippon Kayaku Co., Ltd., naphthol-cresol novolac type epoxy resin), "NC-3000H", "NC-3000", "NC-3000L", "NC-3100" (manufactured by Nippon Kayaku Co., Ltd., biphenyl aralkyl type epoxy resin), "XD-1000-2L", "XD-1000-L", "XD-1000-H", "XD-1000-H" (manufactured by Nippon Kayaku Co., Ltd., dicyclopentadiene type epoxy resin), "ESN475V" (manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., naphthol type epoxy resin), "ESN485" (manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., naphthol novolac type epoxy resin), "YX-4000H", "YX-4000", "YL6121" (manufactured by Mitsubishi Chemical Corporation, biphenyl type epoxy resin), "YX-4000HK" (manufactured by Mitsubishi Chemical Corporation, bixylenol type epoxy resin), "YX-8800" (manufactured by Mitsubishi Chemical Corporation, anthracene type epoxy resin), "PG-100", "CG-500" (manufactured by Osaka Gas Chemicals Co., Ltd., fluorene type epoxy resin), "YL-7760" (manufactured by Mitsubishi Chemical Corporation, bisphenol AF type epoxy resin), "YL-7800" (manufactured by Mitsubishi Chemical Corporation, fluorene type epoxy resin), "jER1010" (manufactured by Mitsubishi Chemical Corporation, solid bisphenol A type epoxy resin), "jER1031S" (manufactured by Mitsubishi Chemical Corporation, tetraphenylethane type epoxy resin), etc. The above may be used alone or in combination of two or more types.

[0074] [Active ester compound]

The active ester compound refers to a compound that contains at least one ester bond in the structure and has aliphatic chains, aliphatic rings, or aromatic rings bonded to both sides of the ester bond. Examples of the active ester compound include compounds having two or more highly reactive ester groups in one molecule, such as phenol esters, thiophenol esters, N-hydroxyamine esters, and esters of heterocyclic hydroxy compounds, and can be obtained by a condensation reaction between at least one compound selected from carboxylic acid compounds, acid chlorides, or thiocarboxylic acid compounds and at least one compound selected from hydroxy compounds or thiol compounds. Particularly, from the viewpoint of improving heat

resistance, it is preferable to obtain from a carboxylic acid compound or an acid chloride and a hydroxy compound, and as the hydroxy compound, a phenol compound or a naphthol compound is preferable. The active ester compound may be used singly or in combination of two or more.

[0075] Examples of the carboxylic acid compound include benzoic acid, acetic acid, succinic acid, maleic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, pyromellitic acid, and the like.

[0076] Examples of the acid chloride include acetyl chloride, acrylic acid chloride, methacrylic acid chloride, malonyl chloride, succinic acid dichloride, diglycolyl chloride, glutaric acid dichloride, suberic acid dichloride, sebacic acid dichloride, adipic acid dichloride, dodecanedioyl dichloride, azelaoyl chloride, 2,5-furandicarbonyl dichloride, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesic acid chloride, bis(4-chlorocarbonylphenyl)ether, 4,4'-diphenyldicarbonyl chloride, 4,4'-azodibenzoyl dichloride, etc.

[0077] Examples of the phenol compound and the naphthol compound include hydroquinone, resorcinol, bisphenol A, bisphenol F, bisphenol S, phenolphthalein, methylated bisphenol A, methylated bisphenol F, methylated bisphenol S, phenol, o-cresol, m-cresol, p-cresol, catechol, α-naphthol, β-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, dihydroxybenzophenone, trihydroxybenzophenone, tetrahydroxybenzophenone, phloroglucinol, benzenetriol, dicyclopentadiene-type diphenol compounds, phenol novolac, phenol resins described later, and the like. Here, "dicyclopentadiene-type diphenol compound" refers to a diphenol compound obtained by condensation of one molecule of dicyclopentadiene with two molecules of phenol.

[0078] Preferable specific examples of the active ester compound include active ester compounds containing a dicyclopentadiene-type diphenol structure, active ester compounds containing a naphthalene structure, active ester compounds containing acetylated products of phenol novolac, active ester compounds containing benzoylated products of phenol novolac,

compounds described in Example 2 of International Publication No. WO2020/095829, compounds disclosed in International Publication No. WO2020/059625, and the like. Among these, active ester compounds containing a naphthalene structure and active ester compounds containing a dicyclopentadiene-type diphenol structure are more preferable. The dicyclopentadiene-type diphenol structure represents a divalent structural unit formed by phenylene-dicyclopentylene-phenylene.

[0079] Examples of commercially available active ester compounds include, as active ester compounds containing a dicyclopentadiene-type diphenol structure, "EXB9451", "EXB9460", "EXB9460S", "HPC-8000-65T", "HPC-8000H-65TM", "EXB-8000L-65TM", "EXB-8150-65T" (manufactured by DIC Corporation), as active ester compounds containing a naphthalene structure, "EXB9416-70BK" (manufactured by DIC Corporation), as active ester compounds containing acetylated products of phenol novolac, "DC808" (manufactured by Mitsubishi Chemical Corporation), as active ester compounds containing benzoylated products of phenol novolac, "YLH1026", "YLH1030", "YLH1048" (manufactured by Mitsubishi Chemical Corporation), as active ester-based curing agents that are acetylated products of phenol novolac, "DC808" (manufactured by Mitsubishi Chemical Corporation), as phosphorus atom-containing active ester-based curing agents, "EXB-9050L-62M" manufactured by DIC Corporation, and the like.

[0080] Regarding the blending ratio of the active ester compound and the epoxy resin, the ratio (α/β) of active ester equivalent (α) to epoxy equivalent (β) is preferably 0.5 to 1.5, more preferably 0.8 to 1.2, and still more preferably 0.90 to 1.10. In the case of being outside the above range, excessive epoxy groups or active ester groups may remain in the system, and there is a risk that properties may deteriorate in a high-temperature storage test (150°C, 1000 hours, etc.) or a long-term reliability test under high-temperature and high-humidity conditions (temperature: 85°C, humidity: 85%, etc.).

[0081] [Phenol resin]

A phenol resin is a compound having two or more phenolic hydroxyl groups in the molecule. Examples of the phenol resin include, but are not limited to, reaction products of phenols and aldehydes, reaction products of phenols and diene compounds, reaction products of phenols and ketones, reaction products of phenols and substituted biphenyls, reaction products of phenols and substituted phenyls, reaction products of bisphenols and aldehydes, and the like. The above may be used alone or in combination of multiple types.

Specific examples of the above raw materials are illustrated below. However, the invention is not limited thereto.

[Phenols]

Phenol, alkyl-substituted phenol, aromatic-substituted phenol, hydroquinone, resorcinol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted dihydroxybenzene, dihydroxynaphthalene, and the like.

<Aldehydes>

Formaldehyde, acetaldehyde, alkyl aldehyde, benzaldehyde, alkyl-substituted benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde, crotonaldehyde, cinnamaldehyde, furfural, and the like.

<Diene compounds>

Dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, and the like.

<Ketones>

Acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, fluorenone, and the like.

<Substituted biphenyls>

4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 4,4'-bis(hydroxymethyl)-1,1'-biphenyl, and the like.

<Substituted phenyls>

1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene, 1,4-bis(hydroxymethyl)benzene, and the like.

[0082] [Polyphenylene ether compounds]

As the polyphenylene ether compound, from the viewpoint of heat resistance and electrical properties, a polyphenylene ether compound having an ethylenic unsaturated bond is preferable, and a polyphenylene ether compound having an acrylic group, methacrylic group, or styrene structure is more preferable. Examples of commercially available products include SA-9000 (manufactured by SABIC, polyphenylene ether compound having a methacrylic group) and OPE-2St 1200 (manufactured by Mitsubishi Gas Chemical Company, polyphenylene ether compound having a styrene structure).

The number average molecular weight (Mn) of the polyphenylene ether compound is preferably 500 to 5000, more preferably 2000 to 5000, and more preferably 2000 to 4000. In the case where the molecular weight is less than 500, there is a tendency that sufficient heat resistance of the cured product cannot be obtained. Moreover, in the case where the molecular weight is greater than 5000, the melt viscosity increases and sufficient fluidity cannot be obtained, so there is a tendency for molding defects to occur easily. In addition, the reactivity also decreases, a long time is required for the curing reaction, and unreacted materials that are not incorporated into the curing system increase, causing the glass transition temperature of the cured product to decrease and the heat resistance of the cured product to decrease.

In the case where the number average molecular weight of the polyphenylene ether compound is 500 to 5000, excellent heat resistance and moldability can be exhibited while excellent dielectric properties are retained. The number average molecular weight herein can be specifically

measured using gel permeation chromatography or the like.

[0083] The polyphenylene ether compound may be one obtained by a polymerization reaction, or one obtained by a redistribution reaction of a high molecular weight polyphenylene ether compound having a number average molecular weight of about 10000 to 30000. Moreover, using these as raw materials, radical polymerizability may be imparted by reacting with a compound having an ethylenic unsaturated bond such as methacryl chloride, acryl chloride, chloromethylstyrene, and the like. The polyphenylene ether compound obtained by redistribution reaction is obtained, for example, by heating a high molecular weight polyphenylene ether compound in a solvent such as toluene in the presence of a phenolic compound and a radical initiator to cause redistribution reaction. The polyphenylene ether compound obtained by redistribution reaction in this manner is preferable because it has hydroxyl groups derived from phenolic compounds that contribute to curing at both ends of the molecular chain, thereby being able to maintain even higher heat resistance, and because functional groups can be introduced at both ends of the molecular chain even after modification with compounds having ethylenic unsaturated bonds. Moreover, the polyphenylene ether compound obtained by polymerization reaction is preferable from the point of showing excellent fluidity.

[0084] The adjustment of the molecular weight of the polyphenylene ether compound can be performed by adjusting polymerization conditions and the like in the case where a polyphenylene ether compound obtained by polymerization reaction. Moreover, in the case where a polyphenylene ether compound is obtained by thereddistribution reaction, the molecular weight of the obtained polyphenylene ether compound can be adjusted by adjusting the conditions of the redistribution reaction and the like. More specifically, adjusting the blending amount of the phenolic compound used in the redistribution reaction can be considered. That is, the greater the blending amount of the phenolic compound, the lower the molecular weight of the obtained polyphenylene ether compound becomes. At this time, as the high molecular weight

polyphenylene ether compound that undergoes redistribution reaction, poly(2,6-dimethyl-1,4-phenylene ether) and the like can be used. Moreover, the phenolic compound used in the redistribution reaction is not particularly limited, but for example, multifunctional phenolic compounds having two or more phenolic hydroxyl groups in the molecule, such as bisphenol A, phenol novolac, cresol novolac, and the like, are preferably used. These may be used alone or in combination of two or more types.

[0085] [Amine resins]

An amine resin is a compound having two or more amino groups in the molecule. Examples of amine resins include diaminodiphenylmethane, diaminodiphenylsulfone, isophoronediamine, naphthalenediamine, aniline novolac (reaction product of aniline and formalin), N-methylaniline novolac (reaction product of N-methylaniline and formalin), orthoethylaniline novolac (reaction product of orthoethylaniline and formalin), reaction product of 2-methylaniline and formalin, reaction product of 2,6-diisopropylaniline and formalin, reaction product of 2,6-diethylaniline and formalin, reaction product of 2-ethyl-6-ethylaniline and formalin, reaction product of 2,6-dimethylaniline and formalin, aniline resin obtained by reaction of aniline and xylylene chloride, reaction product of aniline and substituted biphenyls (4,4'-bis(chloromethyl)-1,1'-biphenyl and 4,4'-bis(methoxymethyl)-1,1'-biphenyl, etc.) described in Japanese Patent No. 6429862, reaction products of aniline and substituted phenyls (1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene and 1,4-bis(hydroxymethyl)benzene, etc.), 4,4'-(1,3-phenylenediisopropylidene)bisaniline, 4,4'-(1,4-phenylenediisopropylidene)bisaniline, reaction product of aniline and diisopropenylbenzene, dimer diamine, and the like, but are not limited thereto. The above may be used alone or in combination of multiple types.

[0086] [Compound containing ethyelenic unsaturated bond]

The compound containing an ethylenic unsaturated bond is a compound having an ethylenic unsaturated bond that can be polymerized by heat or light.

Examples of the compound containing an ethylenic unsaturated bond include the reaction products of the phenol resin and a halogen-based compound containing an ethylenic unsaturated bond (chloromethylstyrene, allyl chloride, methallyl chloride, acrylic acid chloride, methacrylic acid chloride, etc.), reaction products of phenols containing ethylenic unsaturated bonds (2-allylphenol, 2-propenylphenol, 4-allylphenol, 4-propenylphenol, eugenol, isoeugenol, etc.,) and halogen-based compounds (1,4-bis(chloromethyl)benzene, 4,4'-bis(chloromethyl)biphenyl, 4,4'-difluorobenzophenone, 4,4'-dichlorobenzophenone, 4,4'-dibromobenzophenone, cyanuric chloride, etc.), reaction products of epoxy resin or alcohols and (meth)acrylic acids (acrylic acid, methacrylic acid, etc.), and acid-modified products thereof. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0087] [Isocyanate resins]

The isocyanate resin is a compound having two or more isocyanate groups in the molecule. Examples of the isocyanate resin include aromatic diisocyanates such as p-phenylene diisocyanate, m-phenylene diisocyanate, p-xylene diisocyanate, m-xylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and naphthalene diisocyanate; aliphatic or alicyclic diisocyanates such as isophorone diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, hydrogenated xylene diisocyanate, norbornene diisocyanate, and lysine diisocyanate; polyisocyanates such as biuret forms of one or more types of isocyanate monomers or isocyanate forms obtained by trimerizing the above diisocyanate compounds; and polyisocyanates obtained by urethanization reaction of the above isocyanate compounds with polyol compounds. However, the invention is not limited thereto. The above may be used alone or in combination of multiple types.

[0088] [Polyamide resins]

Examples of the polyamide resin include reaction products of one or more of diamine, diisocyanate, and oxazoline with dicarboxylic acid, reaction products of diamine and acid chloride,

and ring-opening polymers of lactam compounds. The above may be used alone or in combination of multiple types.

Specific examples of the above raw materials are illustrated below. However, the invention is not limited thereto.

<Diamine>

Ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decanediamine, undecanediamine, dodecanediamine, tridecanediamine, tetradecanediamine, pentadecanediamine, hexadecanediamine, heptadecanediamine, octadecanediamine, nonadecanediamine, eicosanediamine, 2-methyl-1,5-diaminopentane, 2-methyl-1,8-diaminooctane, dimer diamine, cyclohexanediamine, bis-(4-aminocyclohexyl)methane, bis(3-methyl-4-aminocyclohexyl)methane, xylylenediamine, norbornanediamine, isophoronediamine, bisaminomethyltricyclodecane, phenylenediamine, diethyltoluenediamine, naphthalenediamine, diaminodiphenylmethane, bis(4-amino-3,5-dimethylphenyl)methane, bis(4-amino-3,5-diethylphenyl)methane, 4,4'-methylenebis-o-toluidine, 4,4'-methylenebis-o-ethylaniline, 4,4'-methylenebis-2-ethyl-6-methylaniline, 4,4'-methylenebis-2,6-diisopropylaniline, 4,4-ethylenedianiline, diaminodiphenylsulfone, diaminodiphenyl ether, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 4,4-bis(4-aminophenoxy)biphenyl, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, bis[4-(4-aminophenoxy)phenyl]sulfone, 2,2-bis(3-amino-4-hydroxyphenyl)propane, 2,2-bis(4-aminophenyl)hexafluoropropane, 4,4'-(1,3-phenylenediisopropylidene)bisaniline, 4,4'-(1,4-phenylenediisopropylidene)bisaniline, 9,9-bis(4-aminophenyl)fluorene, 2,7-diaminofluorene, aminobenzylamine, diaminobenzophenone, etc.

<Diisocyanate>

Benzene diisocyanate, toluene diisocyanate, 1,3-bis(isocyanatomethyl)benzene, 1,3-bis(isocyanatomethyl)cyclohexane, bis(4-isocyanatophenyl)methane, isophorone diisocyanate,

1,3-bis(2-isocyanato-2-propyl)benzene, 2,2-bis(4-isocyanatophenyl)hexafluoropropane, dicyclohexylmethane-4,4'-diisocyanate, etc.

<Dicarboxylic acids>

Oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, terephthalic acid, isophthalic acid, 5-hydroxyisophthalic acid, 2-chloroterephthalic acid, 2-methylterephthalic acid, 5-methylisophthalic acid, 5-sodium sulfoisophthalic acid, hexahydroterephthalic acid, hexahydroisophthalic acid, cyclohexanedicarboxylic acid, biphenyldicarboxylic acid, naphthalenedicarboxylic acid, benzophenonedicarboxylic acid, furandicarboxylic acid, 4,4'-dicarboxydiphenyl ether, 4,4'-dicarboxydiphenyl sulfide, etc.

<Acid chlorides>

Acetyl chloride, acrylic acid chloride, methacrylic acid chloride, malonyl chloride, succinic acid dichloride, diglycolyl chloride, glutaric acid dichloride, suberic acid dichloride, sebacic acid dichloride, adipic acid dichloride, dodecanedioyl dichloride, azelaoyl chloride, 2,5-furandicarbonyl dichloride, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesic acid chloride, bis(4-chlorocarbonylphenyl) ether, 4,4'-diphenyldicarbonyl chloride, 4,4'-azodibenzoyl dichloride, etc.

<Lactam>

ε-caprolactam, ω-undecanlactam, ω-laurolactam, etc.

[0089] [Polyimide resins]

Examples of the polyimide resin include, but are not limited to, reaction products of the diamine and tetracarboxylic dianhydrides exemplified below. These may be used alone or multiple types may be used in combination. The above may be used alone or in combination of multiple types.

<Tetracarboxylic dianhydrides>

4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 5-(2,5-dioxotetrahydro-3-furanyl)-3-

methyl-cyclohexene-1,2-dicarboxylic anhydride, pyromellitic dianhydride, 1,2,3,4-benzenetetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,2',3,3'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, methylene-4,4'-diphthalic dianhydride, 1,1-ethylidene-4,4'-diphthalic dianhydride, 2,2'-propylidene-4,4'-diphthalic dianhydride, 1,2-ethylene-4,4'-diphthalic dianhydride, 1,3-trimethylene-4,4'-diphthalic dianhydride, 1,4-tetramethylene-4,4'-diphthalic dianhydride, 1,5-pentamethylene-4,4'-diphthalic dianhydride, 4,4'-oxydiphthalic dianhydride, thio-4,4'-diphthalic dianhydride, sulfonyl-4,4'-diphthalic dianhydride, 1,3-bis(3,4-dicarboxyphenyl)benzene dianhydride, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,3-bis[2-(3,4-dicarboxyphenyl)-2-propyl]benzene dianhydride, 1,4-bis[2-(3,4-dicarboxyphenyl)-2-propyl]benzene dianhydride, bis[3-(3,4-dicarboxyphenoxy)phenyl]methane dianhydride, bis[4-(3,4-dicarboxyphenoxy)phenyl]methane dianhydride, 2,2-bis[3-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, bis(3,4-dicarboxyphenoxy)dimethylsilane dianhydride, 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, 2,3,6,7-anthracenetetracarboxylic dianhydride, 1,2,7,8-phenanthrenetetracarboxylic dianhydride, ethylenetetracarboxylic dianhydride, 1,2,3,4-butanetetracarboxylic dianhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, cyclopentanetetracarboxylic dianhydride, cyclohexane-1,2,3,4-tetracarboxylic dianhydride, cyclohexane-1,2,4,5-tetracarboxylic dianhydride, 3,3',4,4'-bicyclohexyltetracarboxylic dianhydride, carbonyl-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, methylene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, 1,2-ethylene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, 1,1-ethylidene-4,4'-bis(cyclohexane-

1,2-dicarboxylic acid) dianhydride, 2,2-propylidene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, oxy-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, thio-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, sulfonyl-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, rel-[1S,5R,6R]-3-oxabicyclo[3,2,1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione), 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, ethylene glycol-bis-(3,4-dicarboxylic anhydride phenyl) ether, 4,4'-biphenylbis(trimellitic acid monoester acid anhydride), 9,9'-bis(3,4-dicarboxyphenyl)fluorene dianhydride, etc.

[0090] [Maleimide compounds]

The curable resin composition of the embodiment may contain a maleimide compound, for example, 4,4'-diphenylmethane bismaleimide, polyphenylmethane maleimide, m-phenylene bismaleimide, 2,2'-bis[4-(4-maleimidophenoxy)phenyl]propane, 3,3'-dimethyl-5,5'-diethyl-4,4'-diphenylmethane bismaleimide, 4-methyl-1,3-phenylene bismaleimide, 4,4'-diphenyl ether bismaleimide, 4,4'-diphenylsulfone bismaleimide, 1,3-bis(3-maleimidophenoxy)benzene, 1,3-bis(4-maleimidophenoxy)benzene, xylok-type maleimide compound (Anillix Maleimide, manufactured by Mitsui Chemicals Fine Co., Ltd.), biphenyl aralkyl-type maleimide compound (solidified by removing solvent under a reduced pressure from a resin solution containing maleimide compound (M2) described in Example 4 of Japanese Patent Application Laid-Open Publication No. 2009-001783), bisaminocumylbenzene-type maleimide (maleimide compound described in International Publication No. WO 2020/054601), maleimide compound having an indane structure described in Patent No. 6629692 or International Publication No. WO 2020/217679, maleimide compounds described in MATERIAL STAGE Vol.18, No.12 2019 "~Continued Epoxy Resin CAS Number Story~ Curing Agent CAS Number Memorandum No. 31 Bismaleimide (1)" and MATERIAL STAGE Vol.19, No.2 2019 "~Continued Epoxy Resin CAS Number Story~ Curing Agent CAS Number Memorandum No. 32 Bismaleimide (2)", but

are not limited to these. Moreover, these may be used alone or multiple types may be used in combination. The above may be used alone or in combination of multiple types.

[0091] [Cyanate ester resin]

The cyanate ester resin is a cyanate ester compound obtained by reacting a phenol resin with cyanogen halide, and specific examples include: dicyanate benzene, tricyanate benzene, dicyanate naphthalene, dicyanate biphenyl, 2,2'-bis(4-cyanatephenyl)propane, bis(4-cyanatephenyl)methane, bis(3,5-dimethyl-4-cyanatephenyl)methane, 2,2'-bis(3,5-dimethyl-4-cyanatephenyl)propane, 2,2'-bis(4-cyanatephenyl)ethane, 2,2'-bis(4-cyanatephenyl)hexafluoropropane, bis(4-cyanatephenyl)sulfone, bis(4-cyanatephenyl)thioether, phenol novolac cyanate, and products obtained by converting hydroxyl groups of phenol-dicyclopentadiene co-condensates to cyanate groups, but are not limited to these. The above may be used alone or in combination of multiple types.

Moreover, the cyanate esters compound whose synthesis method are described in Japanese Patent Application Laid-Open Publication No. 2005-264154 is particularly preferable as the cyanate ester compound because of the low hygroscopicity, flame retardancy, and dielectric properties.

The cyanate ester resin may contain a catalyst such as zinc naphthenate, cobalt naphthenate, copper naphthenate, lead naphthenate, zinc octylate, tin octylate, lead acetylacetonate, and dibutyltin maleate as needed to trimerize cyanate groups to form a sym-triazine ring.

[0092] The catalyst is preferably used in an amount of 0.0001 to 0.10 parts by mass, preferably 0.00015 to 0.0015 parts by mass, per 100 parts by mass of the cyanate ester resin and the curable resin composition.

[0093] [Polybutadiene and modified products thereof]

Polybutadiene and modified products thereof are polybutadiene or compounds having a structure derived from polybutadiene in the molecule. The structure derived from polybutadiene may have some or all of the unsaturated bonds converted to a single bond by adding hydrogen.

Examples of polybutadiene and modified products thereof include, but are not limited to, polybutadiene, hydroxyl-terminated polybutadiene, terminal (meth)acrylated polybutadiene, carboxylic acid-terminated polybutadiene, amine-terminated polybutadiene, and styrene butadiene rubber. The above may be used alone or in combination of multiple types. Among these, polybutadiene or styrene butadiene rubber is preferable from the viewpoint of dielectric properties. Examples of styrene butadiene rubber (SBR) include RICON-100, RICON-181, RICON-184 (all manufactured by Cray Valley), and 1,2-SBS (manufactured by Nippon Soda Co., Ltd.). Examples of polybutadiene include B-1000, B-2000, and B-3000 (all manufactured by Nippon Soda Co., Ltd.). The molecular weight of polybutadiene and styrene butadiene rubber is preferably a weight average molecular weight of 500 to 10,000, more preferably 750 to 7,500, and even more preferably 1,000 to 5,000. Below the lower limit of the above range, the volatilization amount is large, making it difficult to adjust the solid content during prepreg preparation, and above the upper limit of the above range, the compatibility with other curable resins deteriorates. Generally, in the case where a compound contains hetero atoms such as oxygen and nitrogen like bismaleimide and polymaleimide, due to their polarity, it is difficult to ensure the compatibility with low-polarity compounds such as compounds mainly formed by hydrocarbons or compounds consisting only of hydrocarbons. On the other hand, the compounds of the embodiment, due to the skeletal design that does not actively introduce hetero atoms such as oxygen and nitrogen, also excel in compatibility with materials showing low polarity and low dielectric loss tangent, and compounds consisting only of hydrocarbons.

[0094] [Polystyrene and modified products thereof]

Polystyrene and modified products thereof are polystyrene or compounds having a structure derived from polystyrene in the molecule.

Examples of polystyrene and modified products thereof include, but are not limited to, polystyrene, styrene-2-isopropenyl-2-oxazoline copolymer (Epocros RPS-1005, RP-61, both

manufactured by Nippon Shokubai Co., Ltd.), styrene-ethylene-propylene copolymers (SEPs: Septon 1020 manufactured by Kuraray Co., Ltd.), styrene-ethylene-propylene-styrene copolymers (SEPSs: Septon 2002, Septon 2004F, Septon 2005, Septon 2006, Septon 2063, Septon 2104, all manufactured by Kuraray Co., Ltd.), styrene-ethylene/ethylene-propylene-styrene block copolymer (SEEPS: Septon 4003, Septon 4044, Septon 4055, Septon 4077, Septon 4099, all manufactured by Kuraray Co., Ltd.), styrene-ethylene-butylene-styrene block copolymer (SEBS: Septon 8004, Septon 8006, Septon 8007L, all manufactured by Kuraray Co., Ltd.), compounds having hydroxyl groups at the terminals of styrene-ethylene/ethylene-propylene-styrene block copolymers (SEEPS-OH: Septon HG252 manufactured by Kuraray Co., Ltd.), styrene-isoprene-styrene block copolymer (SIS: Septon 5125, Septon 5127, both manufactured by Kuraray Co., Ltd.), hydrogenated SIS (hydrogenated styrene-isoprene-styrene block copolymer: Hybrar 7125F, Hybrar 7311F, both manufactured by Kuraray Co., Ltd.), styrene-isobutylene-styrene block copolymers: (SIBS: SIBSTAR073T, SIBSTAR102T, SIBSTAR103T (all manufactured by Kaneka Corporation), Septon V9827 (manufactured by Kuraray Co., Ltd.)), etc. The above may be used alone or in combination of multiple types. Polystyrene and modified products thereof preferably do not have unsaturated bonds because they have higher heat resistance and are less susceptible to oxidative degradation. The weight average molecular weight of polystyrene and modified products thereof is not particularly limited as long as the weight average molecular weight is 10,000 or more. Nevertheless, if the weight average molecular weight is too large, the compatibility with the polyphenylene ether compound as well as a low molecular weight component having a weight average molecular weight of about 50 to 1,000 and an oligomer component having a weight average molecular weight of about 1,000 to 5,000 deteriorates, making it difficult to ensure mixing and solvent stability. Therefore, the weight average molecular weight is preferably about 10,000 to 300,000.

[0095] [Polyethylene and modified products thereof]

Polyethylene and the modified products thereof are polyethylene or compounds having a structure derived from polyethylene in the molecule. Polyethylene and the modified products thereof are polyethylene or compounds having a structure derived from polyethylene in the molecule. Examples of polyethylene and the modified products thereof include ethylene-propylene copolymers, ethylene-styrene copolymers, ethylene-propylene-ethylidene norbornene copolymers (EBT manufactured by Mitsui Chemicals: K-8370EM, K-9330M, etc.), ethylene-propylene-vinyl norbornene copolymer (VNB-EPT manufactured by Mitsui Chemicals: PX-006M, PX-008M, PX-009M, etc.), ethylene-vinyl alcohol copolymer, ethylene-vinyl acetate copolymer, etc. However, the invention is not limited thereto. From the viewpoint of improving heat resistance, it is preferable to use an ethylene-propylene-ethylidene norbornene copolymer and an ethylene-propylene-vinyl norbornene copolymer containing crosslinkable structures. The above may be used alone or in combination of multiple types. The weight average molecular weight of polyethylene and the modified products thereof is not particularly limited as long as the weight average molecular weight is 10,000 or more. However, if the weight average molecular weight too large, the compatibility with the polyphenylene ether compound as well as a low molecular weight component having a weight average molecular weight of about 50 to 1,000 and an oligomer component having a weight average molecular weight of about 1,000 to 5,000 deteriorates, making it difficult to ensure mixing and solvent stability. Therefore, the weight average molecular weight is preferably about 10,000 to 300,000.

[0096] The curable resin composition of the embodiment is obtained by preparing the respective components in predetermined proportions, and is pre-cured at 130°C to 180°C for 30 to 500 seconds, and further post-cured at 150°C to 200°C for 2 to 15 hours, whereby sufficient curing reaction proceeds and the cured product of the embodiment is obtained. Moreover, the components of the curable resin composition can be uniformly dispersed or dissolved in a solvent, etc., and be cured after the solvent is removed.

[0097] The preparation method of the curable resin composition of the embodiment is not particularly limited, but each component may be uniformly mixed or may be pre-polymerized. For example, pre-polymerization is performed by heating a mixture in which the compounds of the embodiment are blended in the presence or absence of a curing accelerator or a polymerization initiator, and in the presence or absence of a solvent. Similarly, compounds such as amine compounds, compounds having an ethylenic unsaturated bond, maleimide compounds, cyanate ester compounds, polybutadiene and modified products thereof, polystyrene and modified products thereof, inorganic fillers, and other additives may be added and pre-polymerized. Mixing or pre-polymerization of the respective components is performed by using, for example, an extruder, a kneader, a roll, etc., in the absence of a solvent, and using a reaction vessel equipped with a stirring device, etc., in the presence of a solvent.

[0098] As a method for uniform mixing, mixing is performed in a kneading manner by using a device such as a kneader, a roll, a planetary mixer, etc., at a temperature within the range of 50°C to 100°C to obtain a uniform resin composition. The obtained resin composition is pulverized and then molded into a cylindrical tablet by using a molding machine such as a tablet machine, or made into granular powder or powdered molded bodies, or the compositions can be melted on a surface support and molded into a sheet with a thickness of 0.05 mm to 10 mm to form a curable resin composition molded body. The obtained molded body becomes a molded body that is not sticky at 0°C to 20°C, and shows almost no decrease in fluidity and curability even in the case of being stored at -25°C to 0°C for one week or more.

The obtained molded body can be molded into a cured product by using a transfer molding machine or a compression molding machine.

[0099] The curable resin composition of the embodiment can also be made into a varnish-like composition (hereinafter also simply referred to as varnish) by adding an organic solvent. The curable resin composition of the embodiment is dissolved in a solvent such as toluene, xylene,

acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc., as necessary to form a varnish, which is impregnated into a base material such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, alumina fibers, paper, etc., and is heat-dried to obtain a prepreg. The prepreg is hot-pressed to be molded to form a cured product of the curable resin composition of the embodiment. The solvent used at this time is used in an amount that occupies 10% by weight to 70% by weight, preferably 15% by weight to 70% by weight, in the mixture of the curable resin composition of the embodiment and the solvent. In the case of a liquid composition, a curable resin composition having carbon fibers can also be obtained directly by, for example, the RTM method.

[0100] The curable resin composition of the embodiment can also be used as a modifier for film-type compositions. Specifically, it can be used in the case of improving flexibility in the B-stage. Such film-type resin composition is obtained as a sheet-like adhesive by applying the curable resin composition of the embodiment as the curable resin composition varnish onto a release film, removing the solvent under heating, and then performing B-staging. The sheet-like adhesive can be used as an interlayer insulating layer in a multi-layer substrate, etc.

[0101] The curable resin composition of the embodiment can also be used to obtain a prepreg by heating and melting to reduce viscosity and impregnating reinforcing fibers such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, and alumina fibers. Specific examples thereof include glass fibers such as E glass clothes, D glass clothes, S glass clothes, Q glass clothes, spherical glass clothes, NE glass clothes, and T glass clothes, and further include, in addition to glass, inorganic fibers or organic fibers such as polyparaphenylene terephthalamide (Kevlar (registered trademark), manufactured by DuPont), wholly aromatic polyamide, polyester, polyparaphenylene benzoxazole, polyimide, and carbon fibers. However, the invention is not particularly limited thereto. The shape of the substrate is not particularly limited, and examples include woven fabric, non-woven fabric, roving, and chopped strand mat. As for the weaving

method of woven fabric, plain weave, mock leno weave, twill weave, and the like are known, and these known methods can be appropriately selected and used according to the intended application and performance. Additionally, woven fabric that has been subjected to a fiber opening treatment or glass woven fabric that has been surface-treated with a silane coupling agent or the like is preferably used. The thickness of the substrate is not particularly limited, but is preferably about 0.01 to 0.4 mm. A prepreg can also be obtained by impregnating the reinforced fibers with the varnish and performing heating and drying.

[0102] Additionally, a laminate can be manufactured using the prepreg. The laminate is not particularly limited as long as it includes one or more prepregs, and may have other layers. As a method for manufacturing the laminate, generally known methods can be appropriately applied without particular limitation. For example, in the case of forming a metal foil-clad laminate, a multi-stage press machine, a multi-stage vacuum press machine, a continuous forming machine, an autoclave forming machine, or the like can be used, and a laminate can be obtained by laminating the prepreg and performing molding by heating and pressurizing. At this time, the heating temperature is not particularly limited, but is preferably 65°C to 300°C, and more preferably 120°C to 270°C. The applied pressure is not particularly limited. Nevertheless, if the pressure is too high, it becomes difficult to adjust the solid content of the resin in the laminate and the quality becomes unstable, and if the pressure is too low, air bubbles and adhesion between layers deteriorate, so 2.0 MPa to 5.0 MPa is preferable, and 2.5 MPa to 4.0 MPa is more preferable. The laminate of the embodiment can be suitably used as a metal foil-clad laminate described later by including a layer made of metal foil.

The prepreg is cut into a desired shape, laminated with copper foil, etc., as necessary, and then the curable resin composition is heat-cured while applying pressure to the laminate by press molding, autoclave molding, sheet winding molding, or the like, thereby obtaining a laminate (printed wiring boards) for electrical and electronic component, and/or a carbon fiber reinforced material.

[0103] The curable resin composition of the embodiment can also be made into a resin sheet. As a method for obtaining a resin sheet from the curable resin composition of the embodiment, for example, examples may include a method of applying the curable resin composition on a support film (support), then drying the composition to form a resin composition layer on the support film. In the case where the curable resin composition of the embodiment is used for a resin sheet, it is essential that the film softens under the temperature condition (70°C to 140°C) of lamination in the vacuum lamination method and exhibits fluidity (resin flow) that enables resin filling into via holes or through holes present in the circuit board simultaneously with lamination of the circuit board, and it is preferable to blend the respective components so as to exhibit such properties. In the obtained resin sheet and circuit board (copper-clad laminate, etc.), the uniformity of appearance is required in order to exhibit constant performance at any portion without causing phenomena such as locally different property values due to phase separation or the like.

[0104] Here, the diameter of the through hole of the circuit board is 0.1 mm to 0.5 mm and the depth is 0.1 mm to 1.2 mm, and it is preferable to enable resin filling within this range. In the case of laminating both sides of the circuit board, it is desirable that about 1/2 of the through hole is filled.

[0105] As a specific method for producing the resin sheet, a method can be mentioned in which a varnished resin composition is prepared by blending an organic solvent, then the varnished resin composition is applied to the surface of a support film (Y), and further the organic solvent is dried by heating or hot air blowing etc., to form a resin composition layer (X).

[0106] As the organic solvent used here, for example, it is preferable to use ketones such as acetone, methyl ethyl ketone, and cyclohexanone; acetate esters such as ethyl acetate, butyl acetate, cellosolve acetate, propylene glycol monomethyl ether acetate, and carbitol acetate; carbitols such as cellosolve and butyl carbitol; aromatic hydrocarbons such as toluene and xylene;

dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc., and it is preferable to use them at a ratio that results in a non-volatile content of 30% by mass to 60% by mass.

[0107] The thickness of the resin composition layer (X) to be formed needs to be equal to or greater than the thickness of the conductor layer. Since the thickness of the conductor layer that the circuit board has is in the range of 5 μm to 70 μm, the thickness of the resin composition layer (X) preferably has a thickness of 10 μm to 100 μm. The resin composition layer (X) in the embodiment may be protected by a protective film described later. With the protection of the protective film, the adhesion of dust, etc., to the surface of the resin composition layer and scratches can be prevented.

[0108] The support film and protective film can include polyolefins such as polyethylene, polypropylene, and polyvinyl chloride; polyesters such as polyethylene terephthalate (PET) and polyethylene naphthalate; polycarbonate; polyimide; and further a release paper or a metal foil, such as a copper foil and an aluminum foil. The support film and the protective film may be subjected to a matte treatment, corona treatment, or release treatment. The thickness of the support film is not particularly limited, but is 10 μm to 150 μm, and preferably used in the range of 25 μm to 50 μm. The thickness of the protective film is preferably 1 μm to 40 μm.

[0109] The support film (Y) is peeled off after being laminated to a circuit board or after forming an insulating layer through heating and curing. If the support film (Y) is peeled off after the resin composition layer forming the resin sheet is heat-cured, the adhesion of dust, etc., during the curing process can be prevented. In the case of peeling off after curing, the support film is subjected to a release process in advance.

[0110] A multilayer printed circuit board can be manufactured from the resin sheet obtained as described above. For example, in the case where the resin composition layer (X) is protected by a protective film, after the protective film is peeled off, the resin composition layer (X) is laminated to one side or both sides of the circuit board so as to be in direct contact with the circuit board, for

example, by a vacuum lamination method. The lamination method may be batch-type or continuous-type with rolls. If necessary, the resin sheet and circuit board may be heated (preheated) as needed before performing lamination. Regarding the lamination conditions, the bonding temperature (lamination temperature) is preferably 70°C to 140°C, the bonding pressure is preferably 1 kgf/cm^2 to 11 kgf/cm^2 (9.8×10^4 to $10^7.9\times10^4$ N/m^2), and lamination is preferably performed under a reduced pressure with the air pressure being 20 mmHg (26.7 hPa) or less.

[0111] A semiconductor device can be manufactured by using the curable resin composition of the embodiment. Examples of the semiconductor device include a dual in-line package (DIP), a quad flat package (QFP), a ball grid array (BGA), a chip size package (CSP), a small outline package (SOP), a thin small outline package (TSOP), and a thin quad flat package (TQFP).

[0112] The curable resin composition of the embodiment and the cured product thereof can be used in a wide range of fields. Specifically, the curable resin composition and the cured product thereof can be used for various applications such as molding materials, adhesives, composite materials, and coatings. Since the cured product of the curable resin composition described in the embodiment exhibits excellent heat resistance and dielectric properties, the cured product is suitably used for electrical and electronic components such as a sealing material for semiconductor elements, a sealing material for liquid crystal display elements, a sealing material for organic EL elements, and a laminated board (printed wiring board, BGA substrate, build-up substrates, etc.), composite materials for lightweight high-strength structural materials such as carbon fiber reinforced plastics and glass fiber reinforced plastics, and 3D printing.

[Examples]

[0113] Next, the invention will be described more specifically with examples. Hereinafter, unless otherwise specified, “part” refers to “part by mass”. The invention is not limited to these examples.

[0114] Various analytical methods used in the examples are described below.

・GPC (Gel Permeation Chromatography) Analysis

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

Flow rate: 1.5 ml/min.

Column temperature: 40°C

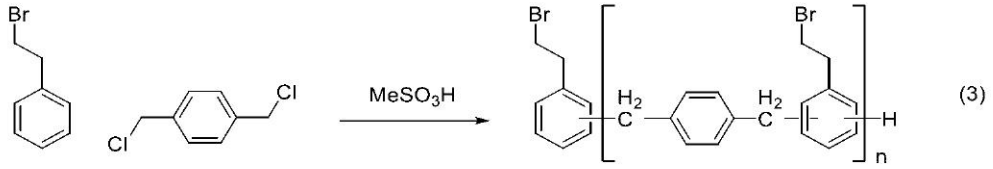
Solvent used: tetrahydrofuran (THF)

Detector: differential refractive index detector (RI)

[0115] [Synthesis Example 1]

A flask equipped with a thermometer, a cooling tube, and a stirrer was fitted with an aspirator and a base trap. To the flask, 370.1 parts of 2-bromoethylbenzene (manufactured by Tokyo Chemical Industry Co., Ltd.), 175.1 parts of α,α'-dichloro-p-xylene (manufactured by Tokyo Chemical Industry Co., Ltd.), and 27.3 parts of methanesulfonic acid (manufactured by Tokyo Chemical Industry Co., Ltd.) were charged, and the mixture was reacted at 130°C for 6 hours while the base trap collected the generated hydrogen chloride. 100 parts of toluene and 600 parts of cyclohexane were added for extraction, and the organic layer was washed 5 times with 100 parts of water. By distilling off the solvent and excess 2-bromoethylbenzene under heating and a reduced pressure, 380 parts of a compound (BEB-1) having a 2-bromoethylbenzene structure represented by the following formula (3) was obtained as a liquid resin (Mn: 938, Mw: 1290). The GPC chart of the obtained compound is shown in FIG. 1. The average value n of the repeating units calculated from the area % of the GPC chart was 2.2.

[0116] [Formula 9]

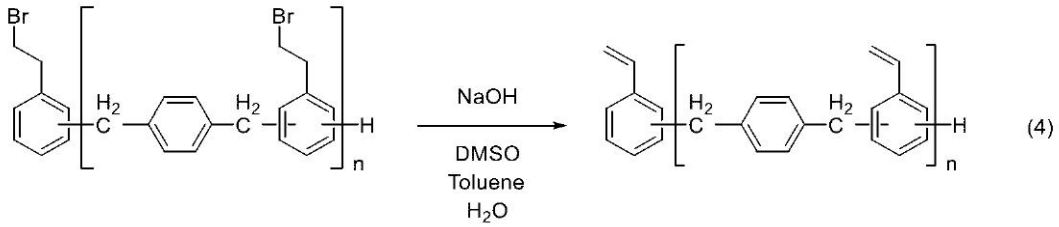


(3)

[0117] [Synthesis Example 2]

To a flask equipped with a thermometer, a cooling tube, and a stirrer, 300 parts of BEB-1 obtained in Synthesis Example 1, 245 parts of toluene, 735 parts of dimethyl sulfoxide, 0.15 parts of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, and 146.4 parts of 50 wt% sodium hydroxide aqueous solution were added, and the reaction was continued at 40°C for 6 hours. 100 parts of water was added, and after the organic layer was washed, the organic layer was returned to the reaction vessel. 735 parts of dimethyl sulfoxide and 9.8 parts of 50 wt% sodium hydroxide aqueous solution were added, and the mixture was reacted again at 40°C for 1 hour. 300 parts of toluene was added, and the organic layer was repeatedly washed with 100 parts of water until the drainage became neutral. The mixture was concentrated under a reduced pressure by using an evaporator to obtain 180 parts of a compound (O-1) having two or more styrene structures in the molecule represented by the following formula (4). The GPC chart of the obtained compound is shown in FIG. 2. Also, the ^{1}H-NMR data (deuterated chloroform) of the obtained compound is shown in FIG. 3. Signals derived from vinyl groups were observed at 5.10 ppm to 5.30 ppm, 5.50 ppm to 5.85 ppm, and 6.60 ppm to .80 ppm in the ^{1}H-NMR chart. The average value n of the repeating units calculated from the area % of the GPC chart was 2.2 (the molecular weight of the resin component was Mn: 797, Mw: 1187).

[0118] [Formula 10]



(4)

[0119] [Example 1, Reference Example 1, Comparative Examples 1-7]

Each polymerization inhibitor and the compound (O-1) obtained in Synthesis Example 2 were blended in the blending amounts shown in Table 1 to prepare toluene solutions with a solid content of 60 wt%. Each solution was stored in a 5 mL glass sample bottle at 40°C for 50 days, and the

case where gelation was visually confirmed were marked with "×", and the case where there was no change in properties was marked as ○. The results are shown in Table 1.

[0120] [Table 1]

		Example 1	Reference Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Compound represented by Formula (1)	O-1	100	100	100	100	100	100	100	100	100
Polymerization inhibitor	MHQ	0.005								
	TBC		0.005							
	HQ				0.005					
	Chimassorb 944 FDL					0.005				
	TEMPOL free radial						0.005			
	Q-1301							0.005		
	AO-60								0.005	
	Irganox - 1010									0.001
	PEP-36									0.002
	AO-412S									0.002
Storage test result		○	○	×	×	×	×	×	×	×

[0121] MHQ: methylhydroquinone (manufactured by Seiko Chemical Co., Ltd.)

TBC: 4-tert-butylcatechol (manufactured by TCI Co., Ltd.)

HQ: hydroquinone (manufactured by TCI Co., Ltd.)

Chimassorb944FDL: hindered amine light stabilizer (manufactured by BASF SE)

TEMPOL Free Radical: 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl free radical (manufactured by TCI Co., Ltd.)

Q-1301: Ammonium N-Nitrosophenylhydroxylamine

AO-60: Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (manufactured by ADEKA Corporation)

Irganox-1010: Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (manufactured by BASF SE)

PEP-36: 3,9-Bis(2,6-di-tert-butyl-4-methylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (manufactured by ADEKA Corporation)

AO-412S: 2,2-Bis{[3-(dodecylthio)-1-oxopropoxy]methyl}propane-1,3-diyl bis[3-(dodecylthio)propionate] (manufactured by ADEKA Corporation)

[0122] From the results in Table 1, it is confirmed that the curable resin compositions using MHQ and TBC, which exhibited a structure in which two phenolic groups and alkyl groups were substituted on one benzene ring, excel in storage stability.

[0123] [Example 2, Comparative Examples 8, 9]

By using the compound (O-1) obtained in Synthesis Example 2 and the polymerization inhibitor in the amount shown in Table 2, vacuum press molding was performed while sandwiching with mirror-finished copper foil (T4X: manufactured by Fukuda Metal Foil & Powder Co., Ltd.), and curing was performed at 220°C for 2 hours. At this time, a cushion paper with a thickness of 250 μm having the center cut out to 150 mm in length and width was used as a spacer. For evaluation, test pieces were cut to desired sizes using a laser cutter as necessary, and evaluation was performed.

[0124] <Dielectric constant test ・dielectric loss tangent test>

A test was performed by using a 10 GHz cavity resonator manufactured by AET Co., Ltd. at 25°C by the cavity resonator perturbation method. The sample size was 1.7 mm width × 100 mm length, and the test was performed with a thickness of 0.1 mm. The evaluation results are shown in Table 2.

[0125] [Table 2]

		Example 2	Comparative Example 8	Comparative Example 9
Compound represented by Formula (1)	O-1	100	100	100
Polymerization inhibitor	MHQ	0.4		
	TBC			0.4
Evaluation results				
Dielectric constant		2.56	2.5	2.58
Dielectric loss tangent test		0.00180	0.00132	0.00232

[0126] From the results in Table 2, it is confirmed that MHQ exhibited little effect on dielectric properties. On the other hand, it is confirmed that the dielectric properties of TBC deteriorated. It is considered that MHQ can suppress the deterioration of dielectric properties because the phenolic groups were positioned symmetrically, resulting in a small dipole moment.

[0127] [Examples 3 to 5, Comparative Examples 10 to 13]

Differential scanning calorimetry (DSC) was performed using the compound (O-1) obtained in Synthesis Example 2 and polymerization inhibitors in the amounts shown in Table 3.

[0128] <Differential Scanning Calorimetry (DSC)>

A test was performed by using Chip-DSC1 manufactured by LINSEIS. The measurement temperature range was 30°C-300°C, the heating rate was 20°C/min, and the gas flow rate was set for a nitrogen gas at 150 mL/min. The onset temperature (exothermic start temperature) at the start point of the exothermic peak is shown in Table 3.

[0129] [Table 3]

		Example 3	Example 4	Example 5	Comparative Example 10	Comparative Example 11	Comparative Example 12	Comparative Example 13
Compound represented by Formula (1)	O-1	100	100	100	100	100	100	100
Polymerization inhibitor	MHQ	0.4						
	TBHQ		0.4					
	DMHQ			0.4				
	TBC					0.4		
	o-Cresol						0.4	
	HQ							0.4
Evaluation results								
Onset temperature (℃)		170	180	180	140	160	160	160

[0130] TBHQ: tert-butylhydroquinone (manufactured by TCI)

DMHQ: 2,6-dimethylhydroquinone (manufactured by TCI)

o-cresol: manufactured by TCI

[0131] From the results in Table 3, it is confirmed that the curable resin composition of the invention had a DSC exothermic start temperature of 170°C or higher.

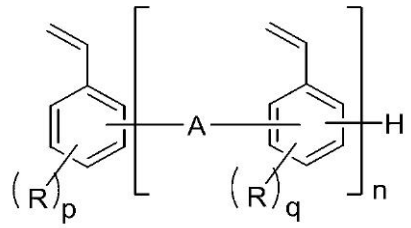
[Industrial Applicability]

[0132] The curable resin composition of the invention is suitably used for electrical and electronic components such as semiconductor encapsulants, printed wiring boards, and build-up laminates.

[Claims]

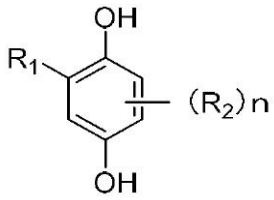
[Claim 1]

A curable resin composition, comprising: a compound represented by Formula (1) and a compound represented by Formula (2),



(1)

wherein in Formula (1), A represents a hydrocarbon group having 1 to 20 carbon atoms, and each of a plurality of R independently represents a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms, and p represents an integer of 0 to 4, q represents an integer of 0 to 3, and n represents an average value for a number of repetitions, which is $1 \leq n \leq 20$, and

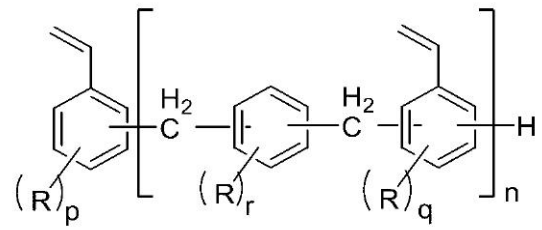


(2)

in Formula (2), each of R_1 and R_2 independently represents a hydrocarbon group having 1 to 20 carbon atoms, and n represents an integer of 0 to 3.

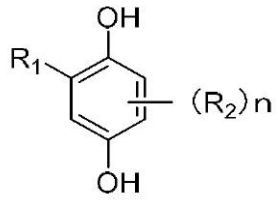
[Claim 2]

A curable resin composition, comprising: a compound represented by Formula (1-1) and a compound represented by Formula (2),



(1-1)

wherein in Formula (1-1) each of a plurality of R independently represents a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms, p and r represent integers of 0 to 4, q represents an integer of 0 to 3, and n represents an average value for a number of repetitions, which is $1 \leq n \leq 20$, and



(2)

in Formula (2), each of R_1 and R_2 independently represents a hydrocarbon group having 1 to 20 carbon atoms, and n represents an integer of 0 to 3.

[Claim 3]

The curable resin composition as claimed in claim 1, comprising a polymerization initiator.

[Claim 4]

The curable resin composition as claimed in claim 1, further comprising at least one selected from a group consisting of a maleimide compound, a polyphenylene ether compound, a compound having an ethylenic unsaturated bond, a cyanate ester resin, polybutadiene and a modified product of polybutadiene, polystyrene and a modified product of polystyrene, polyethylene and a modified product of polyethylene.

[Claim 5]

A cured product, obtained by curing the curable resin composition as claimed in any one of claims 1 to 4.