DESCRIPTION

TITLE OF INVENTION: MALEIMIDE COMPOUND, CURABLE RESIN COMPOSITION AND CURED PRODUCT THEREOF, AMINE COMPOUND AND REACTION PRODUCT OF AMINE COMPOUND WITH MALEIC ANHYDRIDE

TECHNICAL FIELD

[0001]

The present invention relates to a maleimide compound, a curable resin composition and a cured product thereof, as well as an amine compound and a reaction product of the amine compound with maleic anhydride, which are suitable for use in electric and electronic parts such as semiconductor encapsulants, printed wiring boards and build-up laminates, lightweight and high-strength materials such as carbon fiber reinforced plastics and glass fiber reinforced plastics, and 3D printing applications.

BACKGROUND ART

[0002]

In recent years, the laminates on which electric and electronic components are mounted have come to be used in a wider range of fields, and the required characteristics have become more extensive and sophisticated. Conventional semiconductor chips were mainly mounted on metal lead frames, but semiconductor chips with high processing power, such as central processing units (hereinafter referred to as CPUs), are increasingly being mounted on laminates made of polymer materials.

[0003]

In order to satisfy the standard values for characteristics when heated for a heat-resistant laminate, a heat resistance (Tg) of at least 160°C or more is required (Non-Patent Literature 1).

[0004]

In addition, the fifth-generation communication system "5G," which is currently being developed at an accelerated pace, is expected to achieve even greater capacity and faster communication speeds. There is an increasing need for low dissipation factor materials, with a dissipation factor of at least 0.005 at 10 GHz.

[0005]

Furthermore, with the advancement of electronics in the automotive field, precision electronic devices are sometimes placed near the engine drive, requiring higher levels of heat and moisture resistance. SiC semiconductors are beginning to be used in trains and air conditioners, and the encapsulation material for semiconductor elements is now required to have extremely high heat resistance, which is no longer possible with conventional epoxy resin encapsulation materials.

[0006]

In light of this background, polymeric materials that can achieve both heat resistance and low dissipation factor properties have been studied. For example, Patent Literature 1 proposes a composition containing a maleimide resin and a propenyl group-containing phenolic resin. Patent Literature 2 discloses an allyl ether resin in which the hydroxy group is replaced with an allyl group.

[0007]

In recent years, 3D printing has been attracting attention as a method for three-dimensional modeling, and this 3D printing method has begun to be applied in fields that require reliability, such as aerospace, automobiles, and connectors for electronic components used in them. In particular, photocurable and thermosetting resins are being studied for applications such as stereolithography (SLA) and digital light processing (DLP). Therefore, while the conventional method of transferring from a mold mainly requires shape stability and accuracy, 3D printing applications require various properties such as heat resistance, mechanical properties, toughness, flame retardancy, and even electrical properties, and

material development is being promoted. In addition, when used in structural members, property changes due to hygroscopicity, etc. are an issue. Currently, acrylate resins and epoxy resins are used in such applications.

CITATION LIST

PATENT LITERATURE

[0008]

Patent Literature 1: Japanese Patent Publication No. H04 (1992)-359911

Patent Literature 2: International Publication No. 2016/002704

Non-Patent Literature 1: Norio Katayama, "Basic Lecture on Circuit Board Materials, Part 5: Heat-Resistant Glass Epoxy Laminates," Circuit Technology, Japan Institute of Electronics Packaging, 1993, Vol. 8, No. 6, pp. 505-511

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009]

However, in a composition containing a maleimide resin and a propenyl group-containing phenolic resin, phenolic hydroxy groups that do not participate in the curing reaction remain, so the electrical properties are not sufficient.

In addition, it has been shown that Claisen rearrangement occurs at 190°C in an allyl ether resin in which a hydroxy group is substituted with an allyl group, and at 200°C, which is the molding temperature of a general substrate, phenolic hydroxy groups that do not contribute to the curing reaction are generated, so the electrical properties are not satisfactory.

In addition, in the cured product of an acrylate resin or an epoxy resin applied to 3D printing applications, a large number of ester bonds, ether bonds, and even hydroxy groups are contained, and the hygroscopicity properties are insufficient.

[0010]

The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a maleimide compound having high heat resistance, excellent low dielectric properties and good curability, a curable resin composition and a cured product thereof, as well as an amine compound and a reaction product of an amine compound with maleic anhydride which are raw materials thereof.

SOLUTION TO PROBLEM

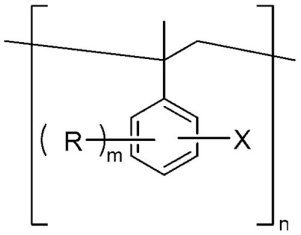
[0011]

That is, the present invention relates to the following [1] to [8]. In the present invention, "(Numerical value 1) to (Numerical value 2)" indicates that the upper and lower limits are included.

[1]

A maleimide compound represented by the following formula (1):

[0012]

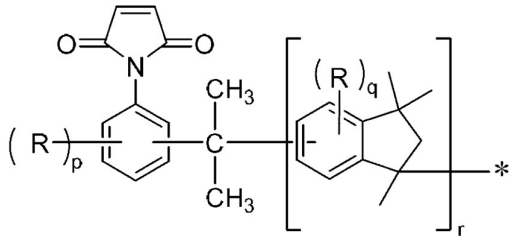


(1)

[0013]

(In formula (1), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. X represents the following formula (2). m is an integer of 0 to 4, n is the number of repetitions, and the average n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$.)

[0014]



(2)

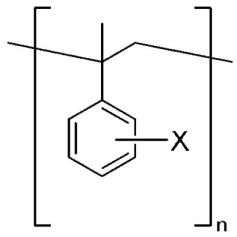
[0015]

(In formula (2), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p represents an integer of 0 to 4, and q represents an integer of 0 to 3. r is the number of repetitions, and the average r_{ave} of r satisfies $1 \leq r_{ave} \leq 20$. * represents a bonding position to the aromatic ring in formula (1).)

[2]

A maleimide compound represented by formula (3) below:

[0016]

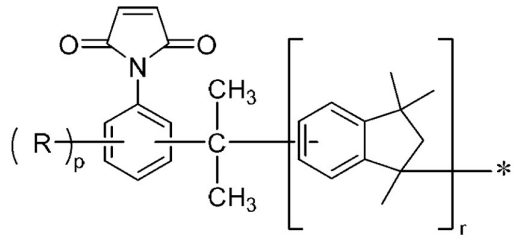


(3)

[0017]

(In formula (3), X represents the following formula (4). n is the number of repetitions, and the average n_{ave} of n satisfies $1.1 \leq n_{ave} \leq 20$.)

[0018]



(4)

[0019]

(In formula (4), each of the multiple R's exists independently and represents a hydrocarbon group having 1 to 5 carbon atoms. p represents an integer of 0 to 4, r is a number of repetitions, and the average r_{ave} of r satisfies $1.1 \leq r_{ave} \leq 20$. * represents a bonding position with the aromatic ring of the compound of formula (3).)

[3]

The maleimide compound according to the above item [2], wherein, in formula (4), p is 2 and the substitution position of R is the ortho position with respect to the maleimide group.

[4]

A curable resin composition comprising the maleimide compound according to any one of the above items [1] to [3].

[5]

The curable resin composition according to the above item [4], further comprising a radical polymerization initiator.

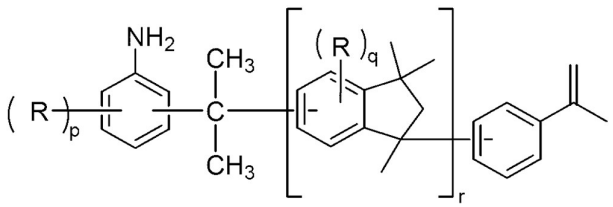
[6]

A cured product obtained by curing the curable resin composition according to the above item [4] or [5].

[7]

An amine compound represented by the following formula (5):

[0020]



(5)

[0021]

(In formula (5), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p represents an integer of 0 to 4, q represents an integer of 0 to 3, r represents the number of repetitions, and the average r_{ave} of r satisfies $1 \leq r_{ave} \leq 20$.)

[8]

A reaction product of the compound according to the preceding item [7] with maleic anhydride.

ADVANTAGEOUS EFFECTS OF INVENTION

[0022]

The cured product of the maleimide compound of the present invention has excellent properties such as high heat resistance and low dielectric properties, and is therefore a useful material for sealing electric and electronic parts, circuit boards, carbon fiber composite materials, etc.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

[Figure 1] A GPC chart of the amine compound of Example 1.

[Figure 2] A GPC chart of the maleimide compound of Example 1.

[Figure 3] A ^{1}H-NMR chart of the maleimide compound of Example 1.

[Figure 4] A GPC chart of the amine compound of Example 2.

[Figure 5] A GPC chart of the maleimide compound of Example 2.

[Figure 6] A ^{1}H-NMR chart of the maleimide compound of Example 2.

[Figure 7] A GPC chart of the amine compound of Synthesis Example 1.

[Figure 8] A GPC chart of the maleimide compound of Synthesis Example 2.

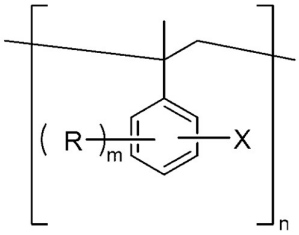
DESCRIPTION OF EMBODIMENTS

[0024]

The maleimide compound of the present embodiment is represented by the following

formula (1).

[0025]

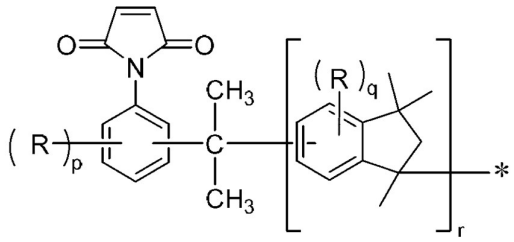


(1)

[0026]

(In formula (1), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. X is represented by the following formula (2). m is an integer of 0 to 4, n is the number of repetitions, and the average n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$.)

[0027]



(2)

[0028]

(In formula (2), each of the multiple R groups exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p represents an integer of 0 to 4, q represents an integer of 0 to 3, r represents a number of repetitions, and the average r_{ave} of r satisfies $1 \leq r_{ave} \leq 20$. * represents the bonding position with the aromatic ring in formula (1).)

[0029]

In the formula (1) and the formula (2), R is a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms, preferably a hydrocarbon group having 1 to 10

carbon atoms, more preferably a hydrocarbon group having 1 to 5 carbon atoms, and particularly preferably a hydrocarbon group having 1 to 3 carbon atoms. When R has a small number of carbon atoms, molecular vibration is unlikely to occur when exposed to high frequency waves. Therefore, when R is a hydrocarbon group having 1 to 3 carbon atoms among the above, the electrical properties are particularly excellent.

[0030]

In the formula (1), m is usually an integer of 0 to 4, preferably 0 to 3, more preferably 0 to 1, and particularly preferably 0. n is the number of repetitions, and the average n_{ave} of n usually satisfies $1 \leq n_{ave} \leq 20$, preferably $1.1 \leq n_{ave} \leq 20$, more preferably $1.1 \leq n_{ave} \leq 18$, and particularly preferably $1.1 \leq n_{ave} \leq 15$. The average n_{ave} of n can be calculated from the value of the number average molecular weight (Mn) obtained by measuring the compound represented by the formula (1) by gel permeation chromatography (GPC), etc. The number average molecular weight is preferably 200 or more and less than 10,000, more preferably 1,000 or more and less than 7,500, and particularly preferably 2,000 or more and less than 5,000. When the number average molecular weight is less than 10,000, purification by washing with water becomes easy, and when it is 200 or more, there is little risk of the target compound volatilizing in the solvent distillation step.

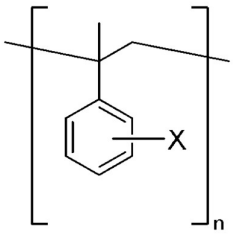
[0031]

In the formula (2), p usually represents an integer of 0 to 4, preferably 0 to 3, and more preferably 0 to 2. q usually represents an integer of 0 to 3, preferably 0 to 2, more preferably 0 to 1, and particularly preferably 0. r is the number of repetitions, and the average r_{ave} of r usually satisfies $1 \leq r_{ave} \leq 20$, preferably $1.1 \leq r_{ave} \leq 20$, more preferably $1.1 \leq r_{ave} \leq 18$, and particularly preferably $1.1 \leq r_{ave} \leq 15$.

[0032]

A preferred embodiment of the maleimide compound represented by the formula (1) is a maleimide compound represented by the following formula (3).

[0033]

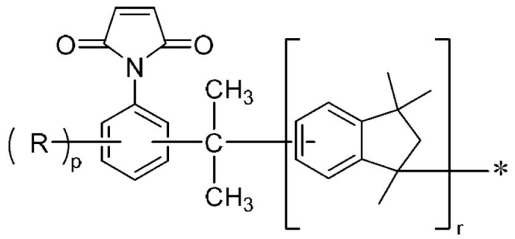


(3)

[0034]

(In formula (3), X is represented by the following formula (4). n is the number of repetitions, and the average n_{ave} of n satisfies $1.1 \leq n_{ave} \leq 20$.)

[0035]



(4)

[0036]

(In formula (4), each of the multiple R's exists independently and represents a hydrocarbon group having 1 to 5 carbon atoms. p represents an integer of 0 to 4, r represents the number of repetitions, and the average r_{ave} satisfies $1.1 \leq r_{ave} \leq 20$. * represents the bonding position with the aromatic ring of the compound of formula (3).)

[0037]

In the formula (4), from the viewpoints of molecular weight control, solvent solubility, dielectric properties, low water absorption, and heat resistance, it is particularly preferable that the ortho positions to the maleimide group are substituted with two Rs.

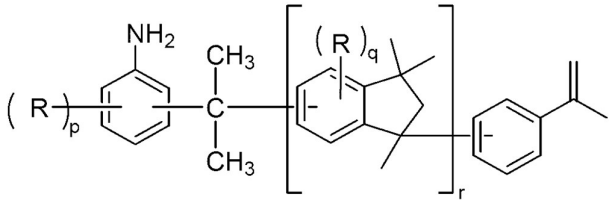
[0038]

The maleimide compound represented by the formula (1) can be obtained, for example, by reacting a polymer of an amine compound represented by the following formula (5) with maleic anhydride. The polymerization of the amine compound represented by the

following formula (5) and the maleimidation reaction may be carried out separately, or the polymerization reaction of the amine compound of the following formula (5) and the maleimidation reaction may be carried out at the same time in the presence of an acid catalyst such as methanesulfonic acid. The conditions for the maleimidation reaction are not particularly limited, and examples of the solvent used include, but are not limited to, water-insoluble solvents such as: 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. Two or more of these may be used in combination. In addition to the water-insoluble solvent, a polar aprotic solvent may also be used in combination. Examples of the polar aprotic solvent include dimethyl sulfone, dimethyl sulfoxide, dimethylformamide, dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, and N-methylpyrrolidone, and two or more of them may be used in combination. When using the polar aprotic solvent, it is preferable to use one with a higher boiling point than the water-insoluble solvent used in combination. In the reaction, as necessary, a catalyst may be used, such as hydrochloric acid, phosphoric acid, sulfuric acid, formic acid, p-toluenesulfonic acid, and methanesulfonic acid; Lewis acids such as aluminum chloride and zinc chloride; solid acids such as activated clay, acidic clay, white carbon, zeolite, and silica alumina; and acidic ion exchange resins. These may be used alone or in combination of two or more. The amount of the catalyst used is usually 0.1 to 0.8 moles, preferably 0.2 to 0.7 moles, per mole of amino group of the amine compound used. If the amount of the catalyst used is too large, the viscosity of the reaction solution may be too high, making stirring difficult, and if the amount is too small, the reaction may proceed slowly. As the co-catalyst for imidization, a basic co-catalyst such as triethylamine can be used alone or in combination. When a sulfonic acid or the like is used as a catalyst, neutralization with an alkali metal such as sodium hydroxide or potassium hydroxide can be performed before proceeding to the extraction step. In the

extraction step, an aromatic hydrocarbon solvent such as toluene or xylene can be used alone, or a non-aromatic hydrocarbon such as cyclohexane or toluene can be used in combination. After extraction, the organic layer is washed with water until the wastewater becomes neutral, and the solvent is distilled off using an evaporator or the like to obtain the target maleimide compound.

[0039]



(5)

[0040]

(In formula (5), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p represents an integer of 0 to 4, q represents an integer of 0 to 3, r represents the number of repetitions, and the average r_{ave} of r satisfies $1 \leq r_{ave} \leq 20$.)

[0041]

The definition of R in the formula (5) and the preferred ranges of p, q and r_{ave} are the same as those in the formula (2).

[0042]

In the formula (5), from the viewpoints of molecular weight control, solvent solubility, dielectric properties, low water absorption, and heat resistance, it is particularly preferable that p=2 and the substitution positions of R are two ortho positions with respect to the amino group in the benzene ring.

[0043]

The softening point of the amine compound represented by the formula (5) is preferably 120°C or less, more preferably 110°C or less. When the softening point is 120°C or

less, the viscosity when derived into the maleimide compound represented by the formula (1) is low. This makes it easy to ensure the fluidity of the curable resin composition, and the impregnation into fibrous materials such as glass cloth and carbon fiber is not impaired, and it is easy to make the curable resin composition semi-cured (B-staged) by prepreg or the like. The viscosity of the curable resin composition can also be reduced by increasing the dilution solvent, but in this case, there is a possibility that the curable resin composition does not sufficiently adhere to the fibrous material in the impregnation step, so it is preferable to make the softening point of the amine compound represented by the formula (5) 120°C or less.

[0044]

The amine compound represented by the formula (5) can be obtained, for example, by reacting anilines with diisopropenylbenzene (or α,α,α',α'-tetramethylbenzene dimethanols) in the presence of an acid catalyst. In this case, the aniline-based compound is preferably unsubstituted or has a substituent of an alkyl group having 1 to 5 carbon atoms, and from the viewpoints of molecular weight control, solvent solubility, dielectric properties, low water absorption, and heat resistance, it is more preferable that the aniline-based compound is unsubstituted or substituted with two alkyl groups having 1 to 3 carbon atoms at the ortho positions of the benzene ring to which the amino group is bonded.

In the synthesis, as the acid catalyst, in addition to liquid acid catalysts such as hydrochloric acid, phosphoric acid, sulfuric acid, formic acid, p-toluenesulfonic acid, and methanesulfonic acid, Lewis acids such as aluminum chloride and zinc chloride, solid acid catalysts such as activated clay, acid clay, white carbon, zeolite, and silica alumina, and acidic ion exchange resins can be used. These acid catalysts may be used alone or in combination of two or more. The amount of the acid catalyst used is 0.01 to 50% by weight, preferably 0.1 to 35% by weight, based on the total weight of the reaction substrates diisopropenylbenzene (or α,α,α',α'-tetramethylbenzene dimethanols) and anilines. If the amount of the acid catalyst used is too large, there is a risk of increasing unnecessary waste, and if the amount is too small,

there is a risk of the reaction proceeding slowly. Examples of the solvent used include, but are not limited to, water-insoluble solvents such as: 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, and two or more of these may be used in combination. In addition to the water-insoluble solvent, a polar aprotic solvent may also be used in combination. For example, dimethyl sulfone, dimethyl sulfoxide, dimethylformamide, dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, N-methylpyrrolidone, and the like may be used in combination of two or more of these. When using a polar aprotic solvent, it is preferable to use one having a higher boiling point than the water-insoluble solvent used in combination. The reaction temperature is preferably 80 to 250°C, more preferably 90 to 240°C, and even more preferably 100 to 230°C. If the reaction temperature is too high, there is a possibility that an unnecessary thermal decomposition reaction will occur, and if the reaction temperature is too low, there is a possibility that the reaction will not proceed sufficiently. When α,α,α',α'-tetramethylbenzene dimethanols are used as raw materials, or when an acid catalyst containing water is used, the generated water and water in the system are removed from the system while azeotroping with the solvent when the temperature is raised. After the reaction is completed, the acid catalyst is neutralized with an alkaline aqueous solution or the like, and then a water-insoluble organic solvent is added to the oil layer and repeatedly washed with water until the wastewater becomes neutral, and then the solvent is removed under heating and reduced pressure. When activated clay or ion exchange resin is used, the reaction liquid is filtered after the reaction is completed to remove the acid catalyst.

[0045]

Examples of the anilines include, but are not limited to, aniline, o-methylaniline, m-methylaniline, p-methylaniline, o-ethylaniline, m-ethylaniline, p-ethylaniline, o-propylaniline,

m-propylaniline, p-propylaniline, o-isopropylaniline, m-isopropylaniline, p-isopropylaniline, 2,6-dimethylaniline, 2,6-diethylaniline, 2,6-dipropylaniline, 2,6-isopropylaniline, 2-ethyl-6-methylaniline, 2-propyl-6-methylaniline, 2-isopropyl-6-methylaniline, 2-ethyl-6-propylaniline, and 2-ethyl-6-isopropylaniline. These may be used alone or in combination of two or more. A larger number of carbon atoms improves solvent solubility but decreases heat resistance, therefore the anilines are preferably unsubstituted or substituted with an alkyl group having 1 to 3 carbon atoms, more preferably unsubstituted or substituted with an alkyl group having 1 to 2 carbon atoms, and most preferably unsubstituted or substituted with a methyl group.

[0046]

Examples of the diisopropenylbenzene include 1,2-diisopropylbenzene, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, and alkyl-substituted derivatives thereof.

Examples of the α,α,α',α'-tetramethylbenzene dimethanols include α,α,α',α'-tetramethyl-1,2-benzene dimethanol, α,α,α',α'-tetramethyl-1,3-benzene dimethanol, α,α,α',α'-tetramethyl-1,4-benzene dimethanol, and alkyl-substituted derivatives thereof.

The diisopropenylbenzene and the α,α,α',α'-tetramethylbenzene dimethanols may be used alone or in combination of two or more. The amount of these used is preferably 1.0 to 10 times the moles, more preferably 1.0 to 7.5 times the moles, and even more preferably 1.0 to 5.0 times the moles, per mole of the amino group of the anilines.

[0047]

[Polymerization initiator]

The curable resin composition of the present embodiment can also improve the curability by adding a polymerization initiator. The polymerization initiator is a compound capable of polymerizing an olefin functional group such as an ethylenically unsaturated bond, and includes an olefin metathesis polymerization initiator, an anionic polymerization initiator, a cationic polymerization initiator, and a radical polymerization initiator. Among these, it is

preferable to use a radical polymerization initiator having curability and moderate stability. In the case of an olefin metathesis polymerization initiator such as a Schrock catalyst having molybdenum as a central metal, an anionic polymerization initiator such as n-butyl lithium (n-BuLi), or a cationic polymerization initiator such as triethylaluminum, they are poor in stability, as they react with moisture in the air.

The radical polymerization initiator is a compound that generates radicals by irradiation with ultraviolet light or visible light or heating, and initiates a chain polymerization reaction. Examples of radical polymerization initiators that can be used include organic peroxides, azo compounds, and benzopinacoles. It is preferable to use an organic peroxide because it has little effect on curing temperature control, outgassing suppression, and electrical properties of decomposition products.

Examples of the organic peroxides include, but are not limited to: 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-butylperoxy-2-ethylhexanoate, t-amylperoxy-3,5,5-trimethylhexanohate, t-butylperoxy-3,5,5-tromethylhexanoate, t-amylperoxybenzoate; peroxycarbonates such as di-2-ethylhexyl peroxydicarbonate, bis(4-t-butylcyclohexyl)peroxydicarbonate, t-butylperoxyisopropyl carbonate, 1,6-bis(t-butylperoxycarbonyloxy)hexane; t-butyl hydroperoxide, cumene hydroperoxide, t-butyl peroxyoctoate, lauroyl peroxide, etc. These may be used alone or in combination. Among the above organic peroxides, ketone peroxides, diacyl peroxides, hydroperoxides, dialkyl peroxides, peroxyketals, alkyl peresters, peroxycarbonates, and the like are preferred, with dialkyl peroxides being more preferred.

Examples of the azo compounds include, but are not limited to, azobisisobutyronitrile, 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis(2,4-dimethylvaleronitrile), and the like. These may be used alone or in combination.

[0048]

The amount of the polymerization initiator added is preferably 0.01 to 5 parts by mass, particularly preferably 0.01 to 3 parts by mass, when the total amount of nonvolatile matters in the curable resin composition excluding the inorganic filler is taken as 100 parts by mass. If the amount of the polymerization initiator used is less than 0.01 part by mass, there is a risk that the molecular weight will not be sufficiently extended during the polymerization reaction, and if it is more than 5 parts by mass, there is a risk that the dielectric properties such as the dielectric constant and the dissipation factor will be impaired.

[0049]

[Polymerization inhibitor]

The curable resin composition of the present embodiment may contain a polymerization inhibitor. By containing a polymerization inhibitor, storage stability is improved and the reaction initiation temperature can be controlled. By controlling the reaction initiation temperature, the fluidity of the curable resin composition can be easily ensured, impregnation into fibrous materials such as glass cloth and carbon fiber is not impaired, and B-stage such as prepreg formation is facilitated. If the polymerization reaction proceeds too much during prepreg formation, problems such as difficulty in lamination during the lamination process are likely to occur.

[0050]

The polymerization inhibitor may be added during or after the synthesis of the compound represented by the formula (1). The amount of the polymerization inhibitor used is 0.008 to 1 part by weight, preferably 0.01 to 0.5 parts by weight, based on 100 parts by weight of the compound represented by the formula (1).

[0051]

Examples of the polymerization inhibitor include phenol-based, sulfur-based, phosphorus-based, hindered amine-based, nitroso-based, and nitroxyl radical-based polymerization inhibitors. The polymerization inhibitor may be used alone or in combination. Among these, in the present embodiment, phenol-based, hindered amine-based, nitroso-based, and nitroxyl radical-based polymerization inhibitors are preferred.

[0052]

Examples of the phenol-based polymerization inhibitor include, but are not limited to: 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, and 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-hydrocinnamamide), 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, bis(3,5-di-t-butyl-4-hydroxybenzylsulfonate ethyl)calcium; and other 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.

[0053]

Examples of the sulfur-based polymerization inhibitor include, but are not limited to, dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, and distearyl-3,3'-thiodipropionate.

[0054]

Examples of the phosphorus-based polymerization inhibitor include, but are not limited to: 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 neopentane tetrayl bis(octadecyl)phosphite, cyclic neopentane tetrayl bis(2,4-di-t-butylphenyl)phosphite, cyclic neopentane tetrayl bis(2,4-di-t-butyl-4-methylphenyl)phosphite, bis[2-t-butyl-6methyl-4-{2-(octadecyloxycarbonyl)ethyl}phenyl]hydrogenphosphite; and 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.

[0055]

Examples of the hindered amine-based polymerization inhibitor include ADK STAB LA-40MP, ADK STAB LA-40Si, ADK STAB LA-402AF, ADK STAB LA-87, ADEKA STAB LA-82, ADEKA STAB LA-81, ADK STAB LA-77Y, ADK STAB LA-77G, ADK STAB LA-72, ADK STAB LA-68, ADK STAB LA-63P, ADK STAB LA-57, ADK STAB L A-52, Chimassorb 2020FDL, Chimassorb 944FDL, Chimassorb 944LD, Tinuvin 622SF, Tinuvin PA144, Tinuvin 765, Tinuvin 770DF, Tinuvin XT55FB, Tinuvin 111FDL, Tinuvin 783FDL, Tinuvin 791FB and the like, but are not limited thereto.

[0056]

Examples of the nitroso-based polymerization inhibitor include, but are not limited to, p-nitrosophenol, N-nitrosodiphenylamine, ammonium salt of N-nitrosophenylhydroxyamine (cupferron), etc. Among these, the ammonium salt of N-

nitrosophenylhydroxyamine (cupferron) is preferred.

[0057]

Examples of the nitroxyl radical polymerization inhibitor include, but are not limited to, 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, etc.

[0058]

[Inorganic filler]

The curable resin composition of the present embodiment may contain an inorganic filler. Examples of inorganic fillers 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; and inorganic fillers obtained by making these into a spherical or crushed shape, but are not limited thereto. In addition, these may be used alone or in combination.

[0059]

When a curable resin composition for semiconductor encapsulation is obtained, the amount of the inorganic filler used is preferably 80 to 92 parts by mass, and more preferably 83 to 90 parts by mass, based on 100 parts by mass of the curable resin composition. When a curable resin composition for an interlayer insulating layer forming material, or a substrate material such as a copper-clad laminate, prepreg, or RCC is obtained, the amount of the inorganic filler used is preferably 5 to 80 parts by mass, and more preferably 10 to 60 parts by mass, based on 100 parts by mass of the curable resin composition.

[0060]

[Curing Accelerator]

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

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, and 1,8-diazabicyclo(5,4,0)-undecene, and 4-dimethylaminopyridine and 1,8-diazabicyclo(5,4,0)-undecene are preferred. Other examples of the cationic curing accelerator include: phosphines such as triphenylphosphine; and quaternary ammonium salts such as tetrabutylammonium salts, triisopropylmethylammonium salts, trimethyldecanylammonium salts, cetyltrimethylammonium salts, and hexadecyltrimethylammonium hydroxide.

Examples of the cationic curing accelerator include: quaternary phosphonium salts such as triphenylbenzylphosphonium salts, triphenylethylphosphonium salts, and tetrabutylphosphonium salts (the counter ions of the quaternary salts are halogens, organic acid ions, hydroxide ions, and the like, and are not particularly specified, but organic acid ions and hydroxide ions are particularly preferred.); and transition metal compounds (transition metal salts) such as tin octylate, zinc carboxylate (zinc 2-ethylhexanoate, zinc stearate, zinc behenate, zinc myristate), and zinc phosphate esters (zinc octylphosphate, zinc stearylphosphate), but are not limited thereto. In addition, these may be used alone or in combination.

[0061]

The amount of the curing accelerator to be blended is 0.01 to 5.0 parts by mass per

100 parts by mass of the total of the nonvolatile contents excluding the inorganic filler in the curable resin composition, as required.

[0062]

[Flame retardant]

The curable resin composition of the present embodiment may contain 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.), and phosphorus-based flame retardants. From the viewpoint of achieving halogen-free flame retardancy, phosphorus-based flame retardants are preferred.

The phosphorus-based flame retardant may be either a reactive type or an additive type. Specific examples include: phosphoric acid esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, cresyl-di-2,6-xylenyl phosphate, 1,3-phenylene bis(dixylenyl phosphate), 1,4-phenylene bis(dixylenyl phosphate), and 4,4'-biphenyl(dixylenyl phosphate); phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide, as well as phosphorus-containing epoxy compounds obtained by reacting an epoxy resin with the active hydrogen of the phosphanes, red phosphorus, and the like, but are not limited thereto. These may be used alone or in combination. Of the above-listed substances, phosphoric acid esters, phosphanes, or phosphorus-containing epoxy compounds are preferred, with 1,3-phenylenebis(dixylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), 4,4'-biphenyl(dixylenyl phosphate) or phosphorus-containing epoxy compounds being particularly preferred.

[0063]

The content of the flame retardant is preferably in the range of 0.1 to 0.6 parts by mass, per 100 parts by mass of the total of the nonvolatile contents excluding the inorganic filler in the curable resin composition. If the content is less than 0.1 part by mass, the flame

retardancy may be insufficient, and if the content is more than 0.6 part by mass, the hygroscopicity and dielectric properties of the cured product may be adversely affected.

[0064]

[Light stabilizer]

The curable resin composition of the present embodiment may contain a light stabilizer. As the light stabilizer, a hindered amine light stabilizer, particularly HALS, etc., is preferable. Examples of HALS include reaction products of dibutylamine, 1,3,5-triazine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl-1,6-hexamethylenediamine and N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, reaction products 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]butyl malonate, 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-butylmalonate bis(1,2,2,6,6-pentamethyl-4-piperidyl) and the like, but are not limited thereto. These may be used alone or in combination.

[0065]

The content of the light stabilizer is preferably in the range of 0.001 to 10 parts by mass, per 100 parts by mass of the total of the non-volatile contents excluding inorganic fillers in the curable resin composition. If the content is less than 0.001 part by mass, it may be insufficient to exhibit a light stabilizing effect, and if the content is more than 10 parts by mass, it may have an adverse effect on the hygroscopicity and dielectric properties of the cured product.

[0066]

[Binder Resin]

The curable resin composition of the present embodiment may use a binder resin. Examples of binder resins include, but are not limited to, butyral resins, acetal resins, acrylic resins, epoxy-nylon resins, NBR-phenol resins, epoxy-NBR resins, and silicone resins. These may be used alone or in combination.

[0067]

The amount of the binder resin is preferably within 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, and more preferably 0.05 to 20 parts by mass, per 100 parts by mass of the total non-volatile content excluding the inorganic filler in the curable resin composition.

[0068]

[Additives]

The curable resin composition of the present embodiment may contain additives, such as modified acrylonitrile copolymers, polyethylene, fluororesins, silicone gels, silicone oils, surface treatment agents for fillers such as silane coupling agents, release agents, and colorants such as carbon black, phthalocyanine blue, and phthalocyanine green.

[0069]

The amount of the additive is preferably 1,000 parts by mass or less, and more preferably 700 parts by mass or less, based on 100 parts by mass of the curable resin composition.

[0070]

The curable resin composition of the present embodiment may further include epoxy resins, active ester compounds, phenolic resins, amine resins, maleimide compounds, compounds having ethylenically unsaturated bonds, isocyanate resins, polyamide resins, polyimide resins, cyanate ester resins, polyphenylene ether compounds, polybutadiene and modified products thereof, polystyrene and modified products thereof, etc., which may be used alone or in combination. Among these compounds, it is preferable to contain compounds

having ethylenically unsaturated bonds, cyanate ester resins, polyphenylene ether compounds, polybutadiene and modified products thereof, and polystyrene and modified products thereof, in view of the balance of heat resistance, adhesion, and dielectric properties. By containing these compounds, the brittleness of the cured product can be improved and adhesion to metals can be improved, and cracks in the package during reliability tests such as solder reflow and thermal cycles can be suppressed.

[0071]

Unless otherwise specified, the amount of the above compounds used is preferably 10 times by mass or less, more preferably 5 times by mass or less, and particularly preferably 3 times by mass or less, relative to the compound represented by formula (1). The preferred lower limit is 0.1 times by mass or more, more preferably 0.25 times by mass or more, and even more preferably 0.5 times by mass or more. By being within the above range, the effects of each compound added can be added while making use of the effects of the heat resistance and dielectric properties of the compound represented by formula (1). As these components, the following examples can be used.

[0072]

[Epoxy resin]

Preferred examples of the epoxy resin are shown below, but are not limited to these. The epoxy resin may be liquid or solid, and may be used alone or in combination.

[0073]

Examples of liquid epoxy resins 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" (all manufactured by Nippon Kayaku Co., Ltd.,

bisphenol A type epoxy resin), "RE303S", "RE304S", "RE403S", "RE404S" (all manufactured by Nippon Kayaku Co., Ltd., bisphenol F type epoxy resin), "HP4032", "HP4032D", "HP4032SS" (all manufactured by DIC Corporation, naphthalene type epoxy resin), "828US", "jER828EL", "825", "828EL" (all manufactured by Mitsubishi Chemical Corporation, bisphenol A type epoxy resin), "jE807", "1750" (all manufactured by Mitsubishi Chemical Corporation, bisphenol F type epoxy resin), "jER152" (manufactured by Mitsubishi Chemical Corporation, phenol Novolac type epoxy resin), "630", "630LSD" (all manufactured by Mitsubishi Chemical Corporation, glycidylamine type epoxy resin), "ZX1059" (manufactured by Nippon Steel & Sumitomo Metal Chemical Co., Ltd., a 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), "Celloxide 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" (all manufactured by Nippon Steel & Sumitomo Metal Chemical Co., Ltd., liquid 1,4-glycidylcyclohexane type epoxy resin), and the like. These may be used alone or in combination of two or more.

[0074]

Preferred examples of solid epoxy resins 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 resins, and examples of such solid epoxy resins 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", and "HP-4710" (all

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" (manufactured by DIC Corporation, dicyclopentadiene type epoxy resin), "HP-7200HH", and "HP-7200H" (all manufactured by DIC Corporation, dicyclopentadiene type epoxy resin), "EXA-7311", "EXA-7311-G3", "EXA-7311-G4", "EXA-7311-G4S", "HP-6000" (all 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" (all manufactured by Nippon Kayaku Co., Ltd., naphthol-cresol novolac type epoxy resin), "NC-3000H", "NC-3000", "NC-3000L", "NC-3100" (all manufactured by Nippon Kayaku Co., Ltd., biphenyl aralkyl type epoxy resin), "XD-1000-2L", "XD-1000-L", "XD-1000-H" (all 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" (all 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. These may be used alone or in combination of two or more.

[0075]

[Active ester compound]

The active ester compound refers to a compound that contains at least one ester bond in the structure and has an aliphatic chain, an aliphatic ring, or an aromatic ring 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 are obtained by a condensation reaction between at least one compound of a carboxylic acid compound, an acid chloride, or a thiocarboxylic acid compound and at least one compound of a hydroxy compound or a thiol compound. In particular, from the viewpoint of improving heat resistance, it is preferable to obtain the active ester compound from a carboxylic acid compound or an acid chloride and a hydroxy compound, and the hydroxy compound is preferably a phenol compound or a naphthol compound. The active ester compound may be used alone or in combination of two or more types.

[0076]

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

[0077]

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, dodecandioyl dichloride, azelaoyl chloride, 2,5-furandicarbonyl dichloride, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesic acid chloride, bis(4-chlorocarbonylphenyl) ether, 4,4'-diphenyldicarbonyl chloride, and 4,4'-azodibenzoyl dichloride.

[0078]

Examples of the phenol compound and naphthol compound include hydroquinone,

resorcin, bisphenol A, bisphenol F, bisphenol S, phenolphthaline, 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, phloroglucin, benzenetriol, dicyclopentadiene-type diphenol compound, phenol novolac, and phenol resins described below. Here, the term "dicyclopentadiene-type diphenol compound" refers to a diphenol compound obtained by condensing one molecule of dicyclopentadiene with two molecules of phenol.

[0079]

Preferred specific examples of the active ester compound include an active ester compound containing a dicyclopentadiene-type diphenol structure, an active ester compound containing a naphthalene structure, an active ester compound containing an acetylated product of phenol novolac, an active ester compound containing a benzoylated product of phenol novolac, a compound described in Example 2 of WO 2020/095829, and a compound disclosed in WO 2020/059625. Among them, an active ester compound containing a naphthalene structure and an active ester compound containing a dicyclopentadiene-type diphenol structure are more preferred. The dicyclopentadiene-type diphenol structure refers to a divalent structural unit consisting of phenylene-dicyclopentylene-phenylene.

[0080]

Commercially available active ester compounds include, for example: active ester compounds containing a dicyclopentadiene-type diphenol structure such as "EXB9451", "EXB9460", "EXB9460S", "HPC-8000-65T", "HPC-8000H-65TM", "EXB-8000L-65TM", and "EXB-8150-65T" (manufactured by DIC Corporation), active ester compounds containing a naphthalene structure such as "EXB9416-70BK" (manufactured by DIC Corporation); active ester compounds containing an acetylated phenol novolac such as "DC808" (manufactured by Mitsubishi Chemical Corporation); active ester compounds

containing a benzoylated phenol novolac such as "YLH1026", "YLH1030", and "YLH1048" (manufactured by Mitsubishi Chemical Corporation); an active ester curing agent which is an acetylated phenol novolac such as "DC808" (manufactured by Mitsubishi Chemical Corporation), and an active ester curing agent containing a phosphorus atom such as "EXB-9050L-62M" (manufactured by DIC Corporation).

[0081]

Regarding a mixing ratio of the active ester compound and the epoxy resin, the ratio (α/β) of the active ester equivalent (α) to the epoxy equivalent (β) is preferably 0.5 to 1.5, more preferably 0.8 to 1.2, and even more preferably 0.90 to 1.10. If it is out of the above range, there is a risk that excess epoxy groups or active ester groups will remain in the system, and the characteristics may deteriorate in a high-temperature storage test (e.g., 150°C, 1000 hours) or a long-term reliability test under high-temperature and high-humidity conditions (e.g., temperature: 85°C, humidity: 85%).

[0082]

[Phenol resin]

Phenol resin is a compound having two or more phenolic hydroxy groups in the molecule. Examples of 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, etc. Furthermore, these may be used alone or in combination.

Specific examples of the above-mentioned raw materials are shown below, but are not limited to these.

<Phenols>

Phenol, alkyl-substituted phenol, aromatic-substituted phenol, hydroquinone, resorcin, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted

dihydroxybenzene, dihydroxynaphthalene, etc.

<Aldehydes>

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

<Diene compounds >

Dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, etc.

<Ketones>

Acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, fluorenone, etc.

<Substituted biphenyls>

4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 4,4'-bis(hydroxymethyl)-1,1'-biphenyl, etc.

<Substituted phenyls>

1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene, 1,4-bis(hydroxymethyl)benzene, etc.

[0083]

[Amine resin]

Amine resin is a compound having two or more amino groups in the molecule. Examples of amine resins include diaminodiphenylmethane, diaminodiphenylsulfone, isophoronediamine, naphthalenediamine, aniline novolak (a reaction product of aniline and formalin), N-methylaniline novolak (a reaction product of N-methylaniline and formalin), orthoethylaniline novolak (a reaction product of orthoethylaniline and formalin), a reaction product of 2-methylaniline and formalin, a reaction product of 2,6-diisopropylaniline and

formalin, a reaction product of 2,6-diethylaniline and formalin, a reaction product of 2-ethyl-6-ethylaniline and formalin, a reaction product of 2,6-dimethylaniline and formalin, and an aniline resin obtained by reacting aniline and xylylene chloride, a reaction product of aniline and a substituted biphenyl (4,4'-bis(chloromethyl)-1,1'-biphenyl and 4,4'-bis(methoxymethyl)-1,1'-biphenyl, etc.) disclosed in Japanese Patent No. 6429862, a reaction product of aniline and a substituted phenyl (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, a reaction product of aniline and diisopropenylbenzene, dimer diamine, etc. Furthermore, these may be used alone or in combination.

[0084]

[Maleimide compound other than the maleimide compound represented by formula (1)]

A maleimide compound is a compound having one or more maleimide groups in the molecule. The curable resin composition of the present embodiment may further contain a maleimide compound other than the maleimide compound represented by formula (1). Examples of maleimide compounds other than the maleimide compound represented by formula (1) include, but are not limited to: 4,4'-diphenylmethane bismaleimide, polyphenylmethane maleimide, m-phenylene bismaleimide, 2,2'-bis[4-(4-maleimidophenoxy)phenyl]propane, 3,3'-dimethyl-5,5'-diethyl-4,4'-diphenylmethane bismaleimide, 4-methyl-1,3-phenylene bismaleimide, 4,4'-diphenylether bismaleimide, 4,4'-diphenylsulfone bismaleimide, 1,3-bis(3-maleimidophenoxy)benzene, 1,3-bis(4-maleimidophenoxy)benzene, and Xylox-type maleimide compounds (anilix-maleimide, manufactured by Mitsui Chemicals Fine Co., Ltd.), biphenylaralkyl-type maleimide compound (solidified by distilling off the solvent under reduced pressure from a resin solution containing the maleimide compound (M2) described in Example 4 of JP2009-001783A), bisaminocumylbenzene-type maleimide (maleimide compound described in

WO2020/054601A), maleimide compounds having an indane structure described in JP6629692B or WO2020/217679, maleimide compounds disclosed in “Continued Epoxy Resin CAS Number Story - Hardener CAS Number Memorandum No. 31 Bismaleimide (1)”, MATERIAL STAGE Vol. 18, No. 12, 2019 and “Continued Epoxy Resin CAS Number Story - Hardener CAS Number Memorandum No. 32 Bismaleimide (2)”, MATERIAL STAGE Vol. 19, No. 2, 2019. These compounds may be used alone or in combination.

[0085]

The amount of the maleimide compound other than the maleimide compound represented by formula (1) added is preferably 10 times by mass or less, more preferably 5 times by mass or less, and particularly preferably 3 times by mass or less, relative to the maleimide compound represented by formula (1). The preferred lower limit is 0.01 times by mass or more, and more preferably 0.1 times by mass or more. Within the above range, the effects of the heat resistance, dielectric properties, and low water absorption of the compound represented by formula (1) can be utilized.

[0086]

[Compound containing an ethylenically unsaturated bond]

The compound containing an ethylenically unsaturated bond is a compound that has one or more ethylenically unsaturated bonds in the molecule that can be polymerized by heat or light, regardless of whether a polymerization initiator is used or not.

Examples of the compound containing an ethylenically unsaturated bond include, but are not limited to, a reaction product of the phenol resin with an ethylenically unsaturated bond-containing halogen-based compound (chloromethylstyrene, allyl chloride, methallyl chloride, acrylic acid chloride, methacrylic acid chloride, etc.), a reaction product of an ethylenically unsaturated bond-containing phenol (2-allylphenol, 2-propenylphenol, 4-allylphenol, 4-propenylphenol, eugenol, isoeugenol, etc.) with a halogen-based compound (1,4-bis(chloromethyl)benzene, 4,4'-bis(chloromethyl)biphenyl, 4,4'-difluorobenzophenone,

4,4'-dichlorobenzophenone, 4,4'-dibromobenzophenone, cyanuric chloride, etc.), a reaction product of an epoxy resin or alcohols with (meth)acrylic acids (acrylic acid, methacrylic acid, etc.), and an acid-modified product thereof. In addition, these may be used alone or in combination.

[0087]

[Isocyanate Resin]

An isocyanate resin is a compound having two or more isocyanate groups in the molecule. Examples of the isocyanate resin include, but are not limited to: aromatic diisocyanates such as p-phenylene diisocyanate, m-phenylene diisocyanate, p-xylylene diisocyanate, m-xylylene 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 one or more biuret forms of isocyanate monomers or isocyanate forms obtained by trimerizing the diisocyanate compounds; and polyisocyanates obtained by a urethanization reaction between the isocyanate compounds and polyol compounds. These may be used alone or in combination.

[0088]

[Polyamide resin]

Examples of polyamide resins include reaction products of one or more of diamines, diisocyanates, and oxazolines with dicarboxylic acids, reaction products of diamines with acid chlorides, and ring-opening polymers of lactam compounds. These may be used alone or in combination.

Specific examples of the above-mentioned raw materials are shown below, but are not limited to these.

<Diamines>

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, cyclohexane diamine, bis-(4-aminocyclohexyl)methane, bis(3-methyl-4-aminocyclohexyl)methane, xylylene diamine, norbornane diamine, isophorone diamine, 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, diaminodiphenyl sulfone, 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, and the like.

<Diisocyanates>

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, dodecandioyl 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.

<Lactams>

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

[0089]

[Polyimide resin]

Examples of polyimide resins include, but are not limited to, reaction products of the diamines described above with the following tetracarboxylic dianhydrides. These may be used alone or in combination.

<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'-diphenylsulfone tetracarboxylic 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 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-naphthalene tetracarboxylic dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, 1,2,5,6-naphthalene tetracarboxylic dianhydride, 3,4,9,10-perylene tetracarboxylic dianhydride, 2,3,6,7-anthracene tetracarboxylic dianhydride, 1,2,7,8-phenanthrene tetracarboxylic dianhydride, ethylene tetracarboxylic dianhydride, 1,2,3,4-butane tetracarboxylic dianhydride, 1,2,3,4-cyclobutane tetracarboxylic dianhydride, cyclopentane tetracarboxylic 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 acid dianhydride, rel-[1S,5 R,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'-biphenyl bis(trimellitic acid monoester acid anhydride), 9,9'-bis(3,4-dicarboxyphenyl)fluorene dianhydride, etc.

[0090]

[Cyanate ester resin]

Cyanate ester resin is a cyanate ester compound obtained by reacting a phenol resin with a cyanogen halide, and specific examples thereof include, but are not limited to: dicyanatobenzene, tricyanatobenzene, dicyanatonaphthalene, dicyanatobiphenyl, 2,2'-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)methane, bis(3,5-dimethyl-4-cyanatophenyl)methane, 2,2'-bis(3,5-dimethyl-4-cyanatophenyl)propane, 2,2'-bis(4-cyanatophenyl)ethane, 2,2'-bis(4-cyanatophenyl)hexafluoropropane, bis(4-cyanatophenyl)sulfone, bis(4-cyanatophenyl)thioether, phenol novolac cyanate, and one in which the hydroxy groups of phenol-dicyclopentadiene co-condensates have been converted to cyanate groups. These may be used alone or in combination.

Furthermore, the cyanate ester compound whose synthesis method is described in JP-A-2005-264154 is particularly preferred as the cyanate ester compound because of its low hygroscopicity, excellent 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, dibutyltin maleate, etc., in order to trimerize the cyanate group to form a sym-triazine ring, as necessary.

[0091]

The catalyst is preferably used in an amount of 0.0001 to 0.10 parts by mass, and

more preferably 0.00015 to 0.0015 parts by mass, per 100 parts by mass of the cyanate ester resin.

[0092]

[Polyphenylene ether compound]

As the polyphenylene ether compound, from the viewpoint of heat resistance and electrical properties, a polyphenylene ether compound having an ethylenically unsaturated bond is preferable, and more preferably a polyphenylene ether compound having an acrylic group, a methacrylic group, or a styrene structure is more preferable. Commercially available products include SA-9000 (manufactured by SABIC, a polyphenylene ether compound having a methacrylic group) and OPE-2St 1200 (manufactured by Mitsubishi Gas Chemical Co., Ltd., a 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. If the molecular weight is less than 500, the heat resistance of the cured product tends to be insufficient. In addition, if the molecular weight is more than 5000, the melt viscosity becomes high and sufficient fluidity cannot be obtained, which tends to cause molding defects. In addition, the reactivity is also reduced, the curing reaction takes a long time, and the amount of unreacted material that is not incorporated into the curing system increases, which leads to a decrease in the glass transition temperature of the cured product and a decrease in the heat resistance of the cured product.

If the number average molecular weight of the polyphenylene ether compound is 500 to 5000, excellent heat resistance and moldability can be achieved while maintaining excellent dielectric properties. The number average molecular weight here can be specifically measured using gel permeation chromatography or the like.

[0093]

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 10,000 to 30,000. In addition, these may be used as raw materials and reacted with a compound having an ethylenically unsaturated bond, such as methacryl chloride, acrylic chloride, or chloromethylstyrene, to impart radical polymerizability. The polyphenylene ether compound obtained by the 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 a redistribution reaction. The polyphenylene ether compound obtained by the redistribution reaction in this way has hydroxy groups derived from a phenolic compound that contributes to curing at both ends of the molecular chain, and is therefore preferable in that it can maintain even higher heat resistance, and that functional groups can be introduced at both ends of the molecular chain even after modification with a compound having an ethylenically unsaturated bond. In addition, the polyphenylene ether compound obtained by the polymerization reaction is preferable in that it exhibits excellent fluidity.

[0094]

The molecular weight of the polyphenylene ether compound can be adjusted by adjusting the polymerization conditions, etc., in the case of a polyphenylene ether compound obtained by a polymerization reaction. In addition, in the case of a polyphenylene ether compound obtained by a redistribution reaction, the molecular weight of the obtained polyphenylene ether compound can be adjusted by adjusting the conditions of the redistribution reaction, etc. More specifically, it is possible to adjust the amount of the phenolic compound used in the redistribution reaction. That is, the greater the amount of the phenolic compound, the lower the molecular weight of the obtained polyphenylene ether compound. In this case, poly(2,6-dimethyl-1,4-phenylene ether) or the like can be used as the high molecular weight polyphenylene ether compound that undergoes the redistribution

reaction. In addition, the phenolic compound used in the redistribution reaction is not particularly limited, but for example, a multifunctional phenolic compound having two or more phenolic hydroxy groups in the molecule, such as bisphenol A, phenol novolac, cresol novolac, etc., is preferably used. These may be used alone or in combination of two or more.

[0095]

The content of the polyphenylene ether compound is not particularly limited, but is preferably 5 to 1000 parts by mass, and more preferably 10 to 750 parts by mass, relative to 100 parts by mass of the compound represented by formula (1). When the content of the polyphenylene ether compound is within the above range, it is preferable in that a cured product is obtained that is not only excellent in heat resistance, etc., but also fully exhibits the excellent dielectric properties of the polyphenylene ether compound.

[0096]

[Polybutadiene and its modified products]

Polybutadiene and its modified products are polybutadiene or compounds having a structure derived from polybutadiene in the molecule. Some or all of the unsaturated bonds of the structure derived from polybutadiene may be converted to single bonds by hydrogenation.

Examples of polybutadiene and its modified products include, but are not limited to, polybutadiene, hydroxy-terminated polybutadiene, (meth)acrylate-terminated polybutadiene, carboxylic acid-terminated polybutadiene, amine-terminated polybutadiene, styrene butadiene rubber, etc. Also, these may be used alone or in combination. Of these, polybutadiene or styrene butadiene rubber is preferred from the viewpoint of dielectric properties. Examples of styrene butadiene rubber (SBR) include RICON-100, RICON-181, and RICON-184 (all manufactured by Cray Valley Corporation), 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 amount of volatilization is large, making it difficult to adjust the solid content when preparing the prepreg, and above the upper limit of the above range, the compatibility with other curable resins is deteriorated. In general, in the case of compounds containing heteroatoms such as oxygen and nitrogen, such as bismaleimide and polymaleimide, it is difficult to ensure compatibility with low-polarity compounds such as compounds mainly composed of hydrocarbons or compounds composed only of hydrocarbons due to their polarity. On the other hand, the compound represented by the formula (1) does not have a skeleton design in which heteroatoms such as oxygen and nitrogen are actively introduced, and therefore has excellent compatibility with materials having low polarity and low dielectric properties, and with compounds composed only of hydrocarbons.

[0097]

The content of polybutadiene and modified products thereof is not particularly limited, but is preferably 5 to 1000 parts by mass, and more preferably 10 to 750 parts by mass, relative to 100 parts by mass of the compound represented by formula (1). When the content of polybutadiene and modified products thereof is within the above range, it is preferable in that a cured product is obtained that is not only excellent in heat resistance, etc., but also fully exhibits the excellent dielectric properties of polybutadiene and modified products thereof.

[0098]

[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 polystyrene, styrene-2-isopropenyl-2-oxazoline copolymers (Epocross RPS-1005, RP-61, both manufactured by Nippon Shokubai Co., Ltd.), SEP (styrene-ethylene-propylene copolymer: Septon 1020,

manufactured by Kuraray Co., Ltd.), SEPS (styrene-ethylene-propylene-styrene copolymer: Septon 2002, Septon 2004F, Septon 2005, Septon 2006, Septon 2063, Septon 2104, all manufactured by Kuraray Co., Ltd.), SEEPS (styrene-ethylene/ethylene-propylene-styrene block copolymer: Septon 4003, Septon 4044, Septon 4055, Septon 4077, Septon 4099, all manufactured by Kuraray Co., Ltd.), and SEBS (styrene-ethylene-butylene-styrene block copolymer: Septon 8004, Septon 8006, Septon 8007L, all manufactured by Kuraray Co., Ltd.), SEEPS-OH (styrene-ethylene/ethylene propylene-styrene block copolymer having a hydroxy group at the end: SEPTON HG252, manufactured by Kuraray Co., Ltd.), SIS (styrene-isoprene-styrene block copolymer: SEPTON 5125, SEPTON 5127, manufactured by Kuraray Co., Ltd.), hydrogenated SIS (hydrogenated styrene-isoprene-styrene block copolymer: HYBRAR 7125F, HYBRAR 7311F, manufactured by Kuraray Co., Ltd.), SIBS (styrene-isobutylene-styrene block copolymer: SIBSTAR073T, SIBSTAR102T, SIBSTAR103T (all manufactured by Kaneka Corporation), SEPTON V9827 (manufactured by Kuraray Co., Ltd.)). These may be used alone or in combination. It is preferable that polystyrene and modified products thereof do not have unsaturated bonds in order to have higher heat resistance and less susceptible to oxidative deterioration. The weight average molecular weight of polystyrene and modified products thereof is not particularly limited as long as it is 10,000 or more, but if it is too large, the compatibility with not only polyphenylene ether compounds but also low molecular weight components with a weight average molecular weight of about 50 to 1,000 and oligomer components with a weight average molecular weight of about 1,000 to 5,000 deteriorates, making it difficult to ensure mixing and solvent stability, so it is preferably about 10,000 to 300,000.

[0099]

The content of polystyrene and modified products thereof is not particularly limited, but is preferably 5 to 1000 parts by mass, and more preferably 10 to 750 parts by mass, relative to 100 parts by mass of the compound represented by the formula (1). Styrene and

modified products thereof in the above range are preferable in that a cured product is obtained that is not only excellent in heat resistance, but also fully exhibits the excellent dielectric properties of polystyrene and modified products thereof.

[0100]

The curable resin composition of the present embodiment can be obtained by preparing the above-mentioned components in a predetermined ratio, pre-curing at 130 to 180°C for 30 to 500 seconds, and then post-curing at 150 to 200°C for 2 to 15 hours, whereby a sufficient curing reaction proceeds to obtain a cured product of the present embodiment. Alternatively, the components of the curable resin composition can be uniformly dispersed or dissolved in a solvent or the like, and cured after removing the solvent.

[0101]

The method for preparing the curable resin composition of the present embodiment is not particularly limited, but each component may be mixed uniformly or may be prepolymerized. For example, a mixture of the maleimide compound represented by the formula (1) and other compounds is heated in the presence or absence of a curing accelerator or a polymerization initiator, and in the presence or absence of a solvent to form a prepolymer. Similarly, an amine compound, a compound having an ethylenically unsaturated bond, a maleimide compound other than the maleimide compound represented by the formula (1), a cyanate ester compound, polybutadiene and modified products thereof, polystyrene and modified products thereof, inorganic fillers, and other additives may be added to form a prepolymer. The mixing of each component or prepolymerization is carried out using, for example, an extruder, a kneader, a roll, or the like in the absence of a solvent, and a reaction kettle with a stirrer in the presence of a solvent.

[0102]

As a method of uniform mixing, the materials are mixed at a temperature in the range of 50 to 100°C by kneading with a device such as a kneader, roll, or planetary mixer to obtain

a uniform resin composition. The obtained resin composition is crushed and then molded into a cylindrical tablet shape using a molding machine such as a tablet machine, or into a granular powder or powder compact, or these compositions can be melted on a surface support and molded into a sheet shape with a thickness of 0.05 mm to 10 mm to obtain a molded curable resin composition. The obtained molded body is a non-sticky molded body at 0 to 20°C, and even if stored at -25 to 0°C for one week or more, the flowability and curability are hardly reduced.

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

[0103]

The curable resin composition of the present embodiment can be made into a varnish-like composition (hereinafter, simply referred to as “varnish”) by adding an organic solvent. The curable resin composition of the present embodiment can be dissolved in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide, or N-methylpyrrolidone as necessary to form a varnish, which is then impregnated into a substrate such as glass fiber, carbon fiber, polyester fiber, polyamide fiber, alumina fiber, or paper, and dried by heating to obtain a prepreg, which is then hot-press molded to obtain a cured product of the curable resin composition of the present embodiment. The solvent used in this case is in an amount that occupies 10 to 70% by weight, preferably 15 to 70% by weight, in the mixture of the curable resin composition of the present embodiment and the solvent. In addition, if the composition is in a liquid state, a cured product of the curable resin containing carbon fiber can be obtained as it is, for example, by the RTM method.

[0104]

The curable composition of the present embodiment can also be used as a modifier for a film-type composition. Specifically, it can be used to improve flexibility and the like in

the B-stage. Such a film-type resin composition is obtained as a sheet-like adhesive by applying the curable resin composition of the present embodiment as the curable resin composition varnish onto a release film, removing the solvent under heating, and then performing B-stage formation. This sheet-like adhesive can be used as an interlayer insulating layer in a multilayer substrate or the like.

[0105]

The curable resin composition of the present embodiment can be heated and melted to reduce the viscosity, and impregnated into reinforced fibers such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, and alumina fibers to obtain a prepreg. Specific examples thereof include, but are not particularly limited to: glass fibers such as E glass cloth, D glass cloth, S glass cloth, Q glass cloth, spherical glass cloth, NE glass cloth, and T glass cloth; inorganic fibers other than glass; and organic fibers such as polyparaphenylene terephthalamide (Kevlar (registered trademark), manufactured by DuPont), all aromatic polyamides, polyester, polyparaphenylene benzoxazole, polyimide, and carbon fibers. The shape of the substrate is not particularly limited, but examples thereof include woven fabric, nonwoven fabric, roving, chopped strand mat, and the like. In addition, as the weaving method of the woven fabric, plain weave, mat weave, twill weave, and the like are known, and these known weaves can be appropriately selected and used depending on the intended use and performance. In addition, woven fabrics that have been subjected to fiber opening treatment and glass woven fabrics that have been surface-treated with a silane coupling agent or the like are 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 reinforcing fibers with the varnish and drying the fibers by heating.

[0106]

Moreover, a laminate can be manufactured using the prepreg. The laminate is not particularly limited as long as it has one or more prepregs, and may have any other layer. The

manufacturing method of the laminate can be appropriately applied by a generally known method, and is not particularly limited. For example, when molding a metal foil-clad laminate, a multi-stage press machine, a multi-stage vacuum press machine, a continuous molding machine, an autoclave molding machine, etc. can be used, and the prepregs are laminated together and heated and pressurized to obtain a laminate. At this time, the heating temperature is not particularly limited, but is preferably 65 to 300 °C, and more preferably 120 to 270 °C. In addition, the pressure to be applied is not particularly limited, but if the pressure is too high, it is difficult to adjust the solid content of the resin of the laminate, and the quality is not stable, and if the pressure is too low, air bubbles and adhesion between the laminates are deteriorated, so that 2.0 to 5.0 MPa is preferable, and 2.5 to 4.0 MPa is more preferable. The laminate of this embodiment can be suitably used as a metal foil-clad laminate described later by providing a layer made of metal foil.

The prepreg is cut into a desired shape and laminated with copper foil or the like as necessary. The laminate is then heated and cured while applying pressure thereto by press molding, autoclave molding, sheet winding molding or the like, to obtain an electrical and electronic laminate (printed wiring board) or a carbon fiber reinforced material.

[0107]

The curable resin composition of this embodiment can also be made into a resin sheet. As a method for obtaining a resin sheet from the curable resin composition of this embodiment, for example, a method of applying the curable resin composition onto a support film (support), followed by drying, and forming a resin composition layer on the support film can be mentioned. When the curable resin composition of this embodiment is used for a resin sheet, it is essential that the film softens under the temperature conditions (70°C to 140°C) of lamination in the vacuum lamination method, and simultaneously with lamination of the circuit board, exhibits a fluidity (resin flow) that allows resin filling in via holes or through holes present in the circuit board, and it is preferable to blend each of the above components

so as to express such characteristics. In addition, in the obtained resin sheet or circuit board (copper-clad laminate, etc.), a phenomenon of locally showing different characteristic values due to phase separation or the like does not occur, and a uniform appearance is required so that a constant performance is expressed at any part.

[0108]

Here, the diameter of the through-holes in the circuit board is 0.1 to 0.5 mm, and the depth is 0.1 to 1.2 mm, and it is preferable to make it possible to fill the resin within this range. When laminating both sides of the circuit board, it is preferable to fill about 1/2 of the through-holes.

[0109]

A specific method for producing the resin sheet includes preparing a resin composition varnished by blending an organic solvent, applying the varnished resin composition to the surface of a support film (Y), and then drying the organic solvent by heating or blowing hot air or the like to form a resin composition layer (X).

[0110]

As the organic solvent used here, for example: ketones such as acetone, methyl ethyl ketone, cyclohexanone, etc.; acetate esters such as ethyl acetate, butyl acetate, cellosolve acetate, propylene glycol monomethyl ether acetate, carbitol acetate, etc.; carbitols such as cellosolve, butyl carbitol, etc.; aromatic hydrocarbons such as toluene, xylene, etc.; dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc. are preferably used, and it is also preferable to use the organic solvent in a proportion such that the nonvolatile content is 30 to 60 mass %.

[0111]

The thickness of the resin composition layer (X) formed must be equal to or greater than the thickness of the conductor layer. Since the thickness of the conductor layer of the circuit board is in the range of 5 to 70 μm, the thickness of the resin composition layer (X) is

preferably 10 to 100 μm. The resin composition layer (X) in this embodiment may be protected with a protective film described below. By protecting the resin composition layer with a protective film, it is possible to prevent the adhesion of dirt and the like to the surface of the resin composition layer and scratches.

[0112]

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

[0113]

The support film (Y) is peeled off after laminating the resin composition layer onto a circuit board or after forming an insulating layer by heat curing of the resin composition layer. If the support film (Y) is peeled off after the resin composition layer constituting the resin sheet is heat cured, adhesion of dust and the like during the curing process can be prevented. When peeling off after curing, the support film is previously subjected to a release treatment.

[0114]

A multilayer printed circuit board can be manufactured from the resin sheet obtained as described above. For example, when the resin composition layer (X) is protected by a protective film, the protective film is peeled off, and then the resin composition layer (X) is laminated on one 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 a batch method or a continuous method using a roll. If necessary, the resin sheet and the circuit board

may be heated (preheated) before lamination. The lamination conditions are preferably a pressure bonding temperature (lamination temperature) of 70 to 140°C, a pressure bonding pressure of 1 to 11 kgf/cm^2 (9.8×10^4 to 107.9×10^4 N/m^2), and lamination is preferably performed under reduced pressure of 20 mmHg (26.7 hPa) or less.

[0115]

In addition, the curable resin composition of the present embodiment can be used to manufacture a semiconductor device. Examples of the semiconductor device includes 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), a thin quad flat package (TQFP), etc.

[0116]

The curable resin composition of the present embodiment and its cured product can be used in a wide range of fields. Specifically, it can be used in various applications such as molding materials, adhesives, composite materials, and paints. The cured product of the curable resin composition described in this embodiment exhibits excellent heat resistance and dielectric properties, and is therefore suitable for use in electrical and electronic components such as semiconductor element encapsulants, liquid crystal display element encapsulants, organic EL element encapsulants, laminates (printed wiring boards, BGA substrates, build-up substrates, etc.), carbon fiber reinforced plastics, glass fiber reinforced plastics, and other lightweight and high-strength structural composite materials, 3D printing, etc.

Example

[0117]

The present invention will now be described in more detail with reference to examples. Unless otherwise specified, all parts are by weight. However, the present invention is not limited to these examples.

[0118]

The various analytical methods used in the examples are described below.

・ GPC (gel permeation chromatography) analysis

Weight average molecular weight (Mw) and number average molecular weight (Mn) were calculated based on polystyrene equivalent using a polystyrene standard solution.

GPC: online degassing unit (DGU-20A3R), binary liquid delivery unit (LC-20AD), autosampler (SIL-20AHT), differential refractive index detector (RID-20A), column oven (CTO-20A), system controller (CBM-20A) (all manufactured by Shimadzu Corporation)

Column: Shodex KF-603 x 1, KF-602.5 x 1, KF-602 x 1, KF-601 x 1 (all manufactured by Showa Denko K.K.)

Guard column: Shodex KF-G 4A (manufactured by Showa Denko K.K.)

Connected eluent: tetrahydrofuran

Flow rate: 1.5 ml/min.

Column temperature: 40°C

Detection: RI (differential refractometer)

[0119]

・ ^{1}H-NMR analysis

Equipment: Nuclear magnetic resonance apparatus (JNM-ECS400) manufactured by JEOL Ltd.

[0120]

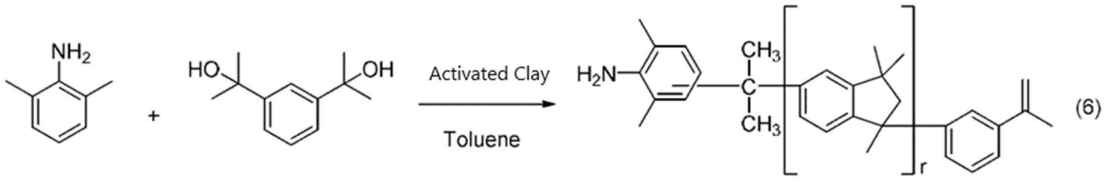
[Example 1]

24.3 parts of 2,6-dimethylaniline, 136 parts of α,α,α',α'-tetramethyl-1,3-benzenedimethanol, 100 parts of toluene, and 35 parts of activated clay were charged into a flask equipped with a thermometer, a condenser, a stirrer, and a Dean-Stark apparatus, and the reaction was carried out for 1.5 hours at an internal temperature of 110 to 135°C while removing the generated water by azeotropic dehydration. Thereafter, the internal temperature was raised to 210°C while extracting toluene, and the reaction was carried out for 4 hours.

After cooling, the extracted toluene was returned to the system, and 200 parts of toluene were newly added. The activated clay was removed by filtration, and a toluene solution (T-1) containing an amine compound represented by the following formula (6) was obtained. The GPC chart of the obtained amine compound is shown in Figure 1.

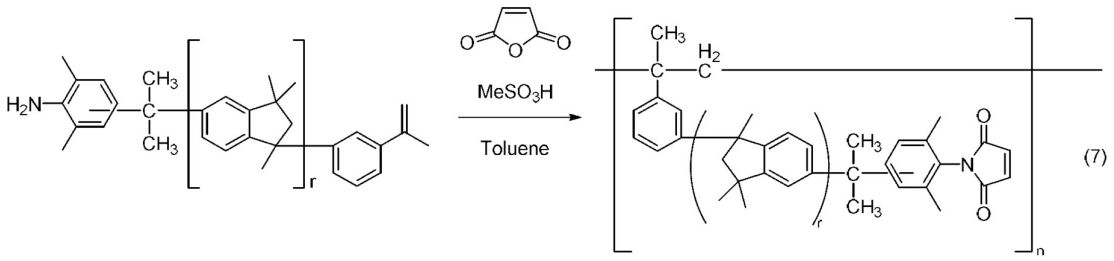
Next, 100 parts of toluene, 29.4 parts of maleic anhydride, and 5.4 parts of methanesulfonic acid were added to a flask equipped with a thermometer, a condenser, a stirrer, and a Dean-Stark apparatus, and T-1 was added dropwise over 4 hours while maintaining the internal temperature at 110°C. Furthermore, a polymerization reaction of the olefin part of the amine represented by the following formula (6) and a maleimidation reaction of the amino group were carried out at 110°C for 9 hours. After cooling, 200 parts of toluene were added, and the organic layer was washed with 100 parts of water five times. The solvent was distilled off under heating and reduced pressure to obtain 133 parts of a maleimide compound (M-1) represented by the following formula (7) as a brown solid resin. The GPC chart of the obtained maleimide compound is shown in Figure 2. The number average molecular weight (Mn) was 2082, and the weight average molecular weight (Mw) was 3169. The ^{1}H-NMR chart (heavy chloroform) of the obtained maleimide compound is shown in Figure 3. A signal derived from the maleimide group was observed at 6.85 ppm in the ^{1}H-NMR chart.

[0121]



(6)

[0122]



(7)

[0123]

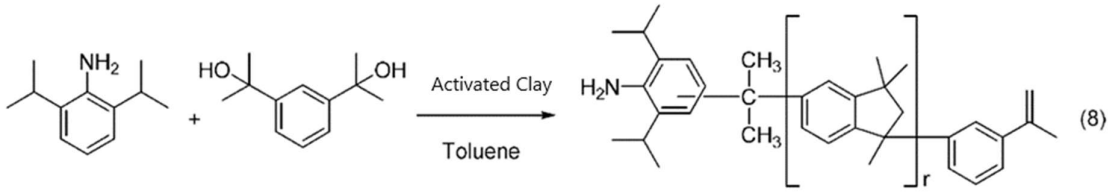
[Example 2]

35.4 parts of 2,6-diisopropylaniline, 136 parts of α,α,α',α'-tetramethyl-1,3-benzenedimethanol, 100 parts of toluene, and 35 parts of activated clay were charged into a flask equipped with a thermometer, a condenser, a stirrer, and a Dean-Stark apparatus, and the reaction was carried out for 2 hours at an internal temperature of 110 to 135°C while removing the generated water by azeotropic dehydration. Thereafter, the internal temperature was raised to 210°C while extracting toluene, and the reaction was carried out for 9 hours. After cooling, the extracted toluene was returned to the system, and 200 parts of toluene were newly added. The activated clay was removed by filtration, and a toluene solution (T-2) containing an amine compound represented by the following formula (8) was obtained. The GPC chart of the obtained amine compound is shown in Figure 4.

Next, 100 parts of toluene, 29.4 parts of maleic anhydride, and 5.4 parts of methanesulfonic acid were added to a flask equipped with a thermometer, a condenser, a stirrer, and a Dean-Stark apparatus, and T-2 was added dropwise over 2 hours while maintaining the internal temperature at 110°C. Furthermore, the polymerization reaction of the olefin part of the amine compound represented by the following formula (8) and the maleimidation reaction of the amino group were carried out at 110°C for 10 hours. After cooling, 200 parts of toluene were added, and the organic layer was washed with 100 parts of water five times. The solvent was distilled off under heating and reduced pressure to obtain 125 parts of a maleimide compound (M-2) represented by the following formula (9) as a

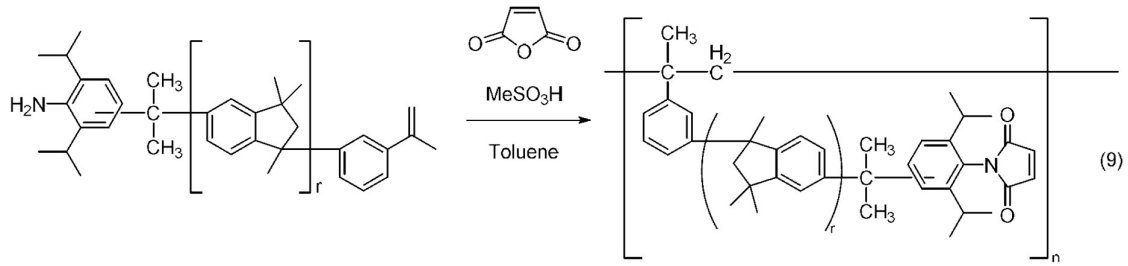
brown solid resin. The GPC chart of the obtained maleimide compound is shown in Figure 5. The number average molecular weight (Mn) was 2007, and the weight average molecular weight (Mw) was 3301. The ^{1}H-NMR chart (heavy chloroform) of the obtained maleimide compound is shown in Figure 6. A signal derived from the maleimide group was observed at 6.85 ppm in the ^{1}H-NMR chart.

[0124]



(8)

[0125]



(9)

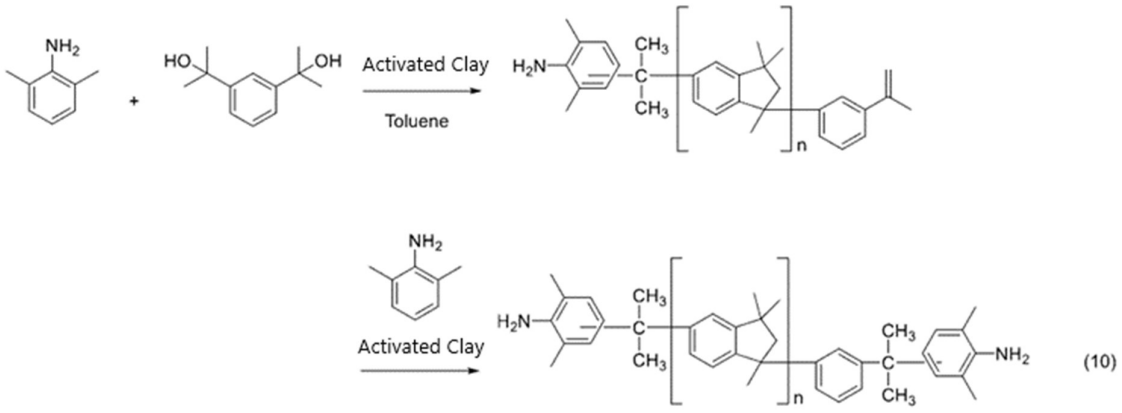
[0126]

[Synthesis Example 1]

48.5 parts of 2,6-dimethylaniline, 155.4 parts of α,α,α',α'-tetramethyl-1,3-benzenedimethanol, 100 parts of toluene, and 30.6 parts of activated clay were charged into a flask equipped with a thermometer, a condenser, a stirrer, and a Dean-Stark apparatus, and the internal temperature was raised to 210°C over 2 hours while removing toluene and the water produced by azeotropic dehydration, and the reaction was carried out for 3 hours (GPC chart is shown in Figure 7). After cooling the internal temperature to 120°C, 145.4 parts of 2,6-dimethylaniline were added, and the reaction was carried out at 220°C for 3 hours. After cooling, the toluene extracted was returned to the system, and 200 parts of toluene were

newly added. The activated clay was removed by filtration, and the solvent and excess 2,6-dimethylaniline were distilled off to obtain 207 parts of amine compound (A-1) represented by the following formula (10) as a brown solid resin (amine equivalent: 272.7 g/eq.). The GPC chart of the obtained amine compound is shown in Figure 7. The number average molecular weight (Mn) was 1048, and the weight average molecular weight (Mw) was 1252.

[0127]



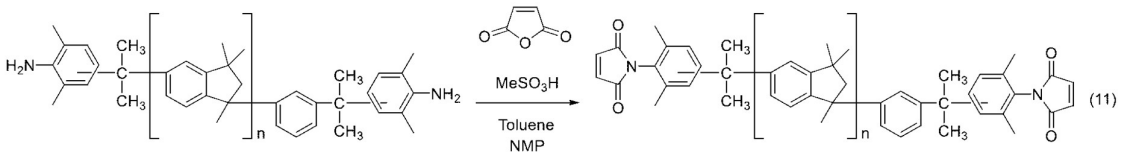
(10)

[0128]

[Synthesis Example 2]

50 parts of toluene, 53.9 parts of maleic anhydride, and 2 parts of methanesulfonic acid were added to a flask equipped with a thermometer, a condenser, a stirrer, and a Dean-Stark apparatus, and a toluene and N-methylpyrrolidone (NMP) solution of A-1 (A-1: 100 parts, toluene: 75 parts, NMP: 25 parts) was added dropwise over 1 hour while maintaining a reflux state. Maleimidation reaction of amino groups was carried out under reflux conditions over 2 hours. After cooling, 100 parts of toluene was added, and the organic layer was washed with 100 parts of water five times. The solvent was distilled off under heating and reduced pressure to obtain 117 parts of a maleimide compound (M-3) represented by the following formula (11) as a brown solid resin. The GPC chart of the obtained maleimide compound is shown in FIG. 8. The number average molecular weight (Mn) was 1353, and the weight average molecular weight (Mw) was 1562.

[0129]



(11)

[0130]

[Examples 3-6, Comparative Example 1]

Each maleimide compound (M-1, M-2, M-3) obtained in Examples 1-2 and Synthesis Example 2, and a thermal radical polymerization initiator DCP (dicumyl peroxide, manufactured by Tokyo Chemical Industry Co., Ltd.) were mixed in the ratios shown in Tables 1 and 2, respectively, and then the mixture was sandwiched between mirror-finished copper foils (T4X: manufactured by Fukuda Metal Copper Foil Co., Ltd.) and vacuum press molded, and cured at 220°C for 2 hours. At this time, a spacer was used in which the center of a 250 μm-thick cushion paper was cut out to 150 mm in length and width. For evaluation, a test piece was cut to the desired size using a laser cutter as necessary, and evaluation was performed. The evaluation results are shown in Tables 1 and 2.

[0131]

<Dielectric constant test/Dissipation factor test>

Tests were performed by a cavity resonator perturbation method using a 10 GHz cavity resonator manufactured by AET Co., Ltd. The test was performed on a sample with a width of 1.7 mm, a length of 100 mm, and a thickness of 0.3 mm.

[0132]

[Table 1]

		Example 3	Example 4	Comparative Exaple 1
Maleimide Compound	M-1	100		
	M-2		100	
	M-3			100
Thermal Radical Polymerization Initiator	DCP	1	1	1
Evaluation Results				
Dielectric Constant (10GHz)		2.35	2.33	2.52
Dissipation Factor (10GHz)		0.0012	0.0011	0.0019

[0133]

<Heat resistance: Differential scanning calorimetry (DSC)>

A differential scanning calorimeter was used to measure the glass transition points Tg of the samples of Examples 5 and 6.

Differential scanning calorimeter: DSC6220 (manufactured by SII NanoTechnology Inc.)

Measurement temperature range: 30 to 330°C

Heating rate: 10°C/min

Atmosphere: Nitrogen (30 mL/min)

Sample amount: 5 mg

Tg: The inflection point on the DSC chart was taken as Tg.

[0134]

[Table 2]

		Example 5	Example 6
Maleimide Compound	M-1	100	
	M-2		100
Thermal Radical Polymerization Initiator	DCP	1	1
Evaluation Results			
Tg (DSC)		243	184

[0135]

From the results in Tables 1 and 2, it was confirmed that the curable resin

composition of the present invention is excellent in dielectric properties and heat resistance.

[0136]

This application claims priority based on Japanese Patent Application No. 2022-052578 filed on March 28, 2022.

INDUSTRIAL APPLICABILITY

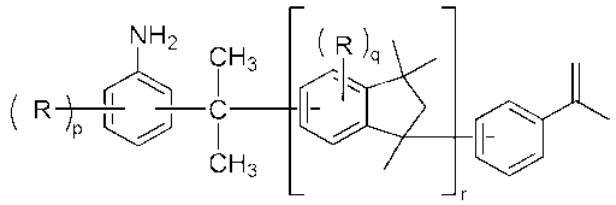
[0137]

The curable resin composition containing the maleimide compound of the present invention and the cured product obtained by curing the same are suitably used for electric and electronic parts such as semiconductor encapsulants, printed wiring boards, and build-up laminates.

Claims

[Claim 1]

An amine compound represented by the following formula (5):



(5)

(In formula (5), each of a plurality of R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p represents an integer of 0 to 4, and q represents an integer of 0 to 3. r is a number of repetitions, and the average r_{ave} of r satisfies $1 \leq r_{ave} \leq 20$.

[Claim 2]

The reaction product of a compound according to claim 1 with maleic anhydride.