Description

Title of Invention: POLYFUNCTIONAL VINYL AROMATIC COPOLYMER, METHOD FOR PRODUCING SAME, CURABLE RESIN COMPOSITION AND CURED PRODUCT OF SAME

Technical Field

[0001]

The present invention relates to a novel polyfunctional vinyl aromatic copolymer, a method for producing the same, and a curable resin composition containing the copolymer.

Background Art

[0002]

Due to a recent increase in information communication volumes, communications of information at high-frequency bands have been actively promoted. In order to achieve more excellent electrical characteristics, particularly to reduce transmission loss at high-frequency bands, there are demands for electrical insulating materials that have low permittivity and low dielectric dissipation factor.

[0003]

Conventionally, thermosetting resins such as phenol resins, epoxy resins and polyimide resins have been used for printed circuit boards. These resins have various properties with balance, but do not have sufficient dielectric properties in a high-frequency range. As new materials that solve the problem, resin compositions containing a radical polymerizable compound and an epoxy resin are disclosed (Patent Literatures 1 and 2).

However, in the resin compositions containing an epoxy resin and a radical

polymerizable compound as disclosed in Patent Literatures 1 and 2, the epoxy resin and the radical polymerizable compound are each independently subjected to a cross-linking reaction, so that two kinds of three-dimensional networks are formed in a cured product. As a result, phase separation occurs in the cured product, a sufficient cross-linking density cannot be obtained, and high mechanical properties are hardly exhibited. Therefore, there is a problem that the addition amount of a vinyl resin having excellent dielectric properties cannot be increased.

[0004]

Patent Literature 3 discloses a polyfunctional vinyl aromatic copolymer having a structural unit derived from a divinyl aromatic compound, as a radical polymerizable compound. This polyfunctional vinyl aromatic copolymers per se have polymerizable double bonds, and therefore curing of such a copolymer provides a cured product having a high glass transition temperature. Therefore, this cured product or polyfunctional vinyl aromatic copolymer can be said as a polymer having excellent heat resistance or a precursor thereof. Further, this polyfunctional vinyl aromatic copolymer is copolymerized with a different radical polymerizable monomer to provide a cured product, and this cured product is also a polymer having excellent heat resistance. However, the copolymer is a compound having only a radical polymerization property, and does not react with an epoxy resin.

Citation List

Patent Literature

[0005]

Patent Literature 1: JP7263069

Patent Literature 2: JP2015-48458 A

Patent Literature 3: WO2018/181842

Summary of Invention

[0006]

The present invention has been made by studying a vinyl resin, particularly a composition of an epoxy resin or the like and a vinyl resin, and it is an object of the present invention to provide a novel polyfunctional vinyl aromatic copolymer that exhibits improved reactivity, and is capable of providing a cured product or molded product having improved uniformity and mechanical properties, and a method for producing the polyfunctional vinyl aromatic copolymer.

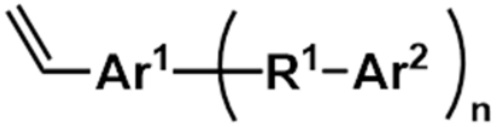
[0007]

The present inventors have intensively studied to achieve the above object and, as a result, have found that a novel polyfunctional vinyl aromatic copolymer having a specific active ester group exhibits improved reactivity in a resin composition of the polyfunctional vinyl aromatic copolymer and an epoxy resin or the like, and is capable of providing a cured product having improved uniformity and excellent mechanical properties. In this way, the present invention has been completed.

[0008]

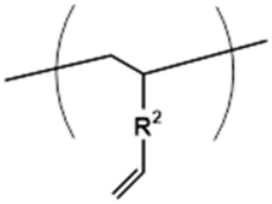
Specifically, the present invention is directed to a polyfunctional vinyl aromatic copolymer obtained by using 2 mol% or more and less than 95 mol% of a divinyl aromatic compound (a), 2 mol% or more and less than 93 mol% of an ester group-containing vinyl aromatic compound (b) represented by the following formula (1), and 5 mol% or more and less than 96 mol% of a structural unit derived from a monovinyl aromatic compound (c), the copolymer containing a structural unit represented by the following formula (a1) derived from the divinyl aromatic compound (a) and a structural unit represented by the following formula (b1) derived from the ester group-containing vinyl aromatic compound (b), having a number-average molecular weight of 300 to 100,000 and a molecular weight distribution

(Mw/Mn), which is represented as a ratio between a weight-average molecular weight and a number-average molecular weight, of 100 or less and being soluble in a solvent:



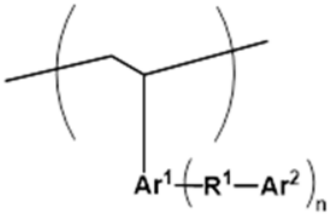
(1)

wherein Ar1 and Ar2 are each independently an aromatic ring group with a benzene ring or a naphthalene ring, and the aromatic ring in each or either of Ar1 and Ar2 contains an ester group having 1 to 15 carbon atoms as a substituent group, and may have an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryl group having 6 to 11 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, an aryloxy group having 6 to 11 carbon atoms, or an aralkyloxy group having 7 to 12 carbon atoms, as a substituent group, R1 is a direct bond, or a divalent group selected from the group consisting of a hydrocarbon group having 1 to 20 carbon atoms, -CO-, -O-, -S-, -SO2- and -C(CF3)2-, and n is 0 to 1,



(a1)

wherein R2 represents an aromatic hydrocarbon group having 6 to 30 carbon atoms,



(b1)

wherein Ar1, Ar2, R1 and n are as defined in the formula (1).

[0009]

The present invention is also directed to a method for producing the polyfunctional vinyl aromatic copolymer, the method including polymerizing a divinyl aromatic compound (a), an ester group-containing vinyl aromatic compound (b) represented by the formula (1) and a monovinyl aromatic compound (c) at a temperature of -20 to 120°C in the presence of a Lewis acid catalyst using the divinyl aromatic compound (a), the ester group-containing vinyl aromatic compound (b) represented by the following formula (1) and the monovinyl aromatic compound (c) in an amount of 2 mol% or more and less than 95 mol%, an amount of 2 mol% or more and less than 93 mol% and an amount of 5 mol% or more and less than 96 mol%, respectively, relative to a sum total of (a), (b) and (c).

In the production method, the Lewis acid catalyst (f) is desirably a metal fluoride or a complex thereof.

[0010]

The present invention is also directed to a curable resin composition containing the polyfunctional vinyl aromatic copolymer and a radical polymerization initiator.

The curable resin composition is also a curable resin composition containing the polyfunctional vinyl aromatic copolymer and an epoxy resin. The epoxy resin preferably has two or more epoxy groups in one molecule thereof.

[0011]

The polyfunctional vinyl aromatic copolymer of the present invention can be subjected to a cross-linking reaction between an active ester group contained in a structural unit represented by the above formula (b1) derived from an ester group-containing vinyl aromatic compound represented by the formula (1) and an epoxy group, and can also be subjected to a cross-linking reaction through a radical polymerization reaction with a vinyl group. Therefore, the polyfunctional vinyl aromatic copolymer of the present invention provides a cured product having

improved uniformity and improved mechanical properties.

Brief Description of Drawings

[0012]

[Figure 1] Figure 1 is an IR chart of a polyfunctional vinyl aromatic copolymer of Example 1.

[Figure 2] Figure 2 is a GPC chart of the polyfunctional vinyl aromatic copolymer of Example 1.

Description of Embodiments

[0013]

The polyfunctional vinyl aromatic copolymer of the present invention contains a structural unit derived from a divinyl aromatic compound (a), contains a structure derived from an ester group-containing vinyl aromatic compound (b) represented by the formula (1), and contains a structural unit derived from a monovinyl aromatic compound (c).

The polyfunctional vinyl aromatic copolymer has a number-average molecular weight Mn of 300 to 100,000 and a molecular weight distribution (Mw/Mn), which is represented as a ratio between a weight-average molecular weight Mw and a number-average molecular weight Mn, of 100 or less, and is soluble in a solvent.

The term "structural unit" used herein includes a repeating unit present in the main chain of the copolymer and a unit or a terminal group present at the terminal or in the side chain.

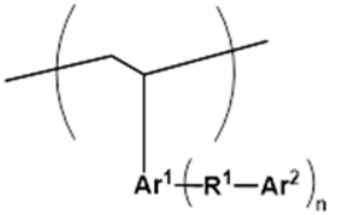
[0014]

A vinyl group constituting the formula (a1) and derived from the divinyl aromatic compound (a) functions as a cross-linking component and contributes to allowing the polyfunctional vinyl aromatic copolymer to exhibit heat resistance.

On the other hand, the structural units derived from the ester group-containing vinyl aromatic compound (b) and the monovinyl aromatic compound (c), in which no vinyl group remains because polymerization is usually considered to proceed through a 1,2-addition reaction of vinyl groups, thus do not function as a cross-linking component with vinyl groups.

[0015]

The structural unit (b1) derived from the ester group-containing vinyl aromatic compound (b) represented by the formula (1), in which an active ester group functions as a cross-linking component through a reaction with an epoxy group, thus improves reactivity in a resin composition of the polyfunctional vinyl aromatic copolymer and an epoxy resin, and contributes to the uniformity and the mechanical properties of a cured product.



(b1)

[0016]

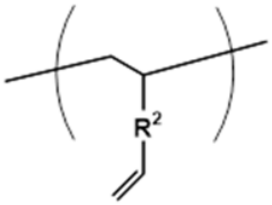
The structural unit derived from the monovinyl aromatic compound (c) does not function as a cross-linking component with vinyl groups and epoxy groups, but is used for adjustment to an arbitrary active ester equivalent and a vinyl equivalent, and contributes to development of molding processability.

[0017]

The structural unit derived from a divinyl aromatic compound (a) is contained in an amount of 2 mol% or more and less than 95 mol% relative to the sum total of the structural units derived from (a), (b), and (c). The structural unit derived from a divinyl aromatic compound (a) can have a plurality of structures such as one formed

by reaction of only one of two vinyl groups and one formed by reaction of two vinyl groups.

Among these, a repeating unit obtained by reaction of only one vinyl group, which is represented by the formula (a1), is preferably contained in an amount of 2 to 80 mol%. More preferred is 5 to 70 mol%, even more preferred is 10 to 60 %, and particularly preferred is 15 to 50 %. When the content of such a repeating unit is 2 to 80 mol%, low dielectric dissipation factor, high toughness, excellent heat resistance, and excellent compatibility with a different resin are achieved. Further, a resulting resin composition is excellent in moist-heat resistance, thermal oxidative deterioration resistance, and molding processability. If the content is less than 2 mol%, heat resistance tends to deteriorate, and if the content exceeds 80 mol%, delamination peel strength of a resulting laminate tends to reduce.



(a1)

[0018]

The structural unit derived from the ester group-containing vinyl aromatic compound (b) represented by the formula (1) is contained in an amount of 2 mol% or more and less than 93 mol% relative to the sum total of the structural units derived from (a), (b) and (c). More preferred is 5 to 80 mol%, even more preferred is 5 to 70 mol%, and particularly preferred is 5 to 60 mol%. If the content of the structural unit derived from the ester group-containing vinyl aromatic compound (b) is less than 2 mol%, there is a tendency that a sufficient cross-linking density cannot be obtained in a resin composition of the polyfunctional vinyl aromatic copolymer and an epoxy resin, and mechanical properties are not improved. If the content of the structural unit derived from the ester group-containing vinyl aromatic compound (b)

is more than 93 mol%, delamination peel strength of a resulting laminate tends to reduce. Substantially the total amount of the structural unit derived from the ester group-containing vinyl aromatic compound (b) represented by the formula (1) is constituted by the structural unit represented by the formula (b1).

[0019]

The structural unit derived from the monovinyl aromatic compound (c) is contained in an amount of 5 mol% or more and less than 96 mol% relative to the sum total of the structural units derived from (a), (b) and (c). Preferred is 10% to 80%, and more preferred is 15% to 70%. If the mole fraction of the structural units derived from (b) and (c) is less than 0.05, molding processability is poor, and if the content of (c) exceeds 98%, a cured product is poor in heat resistance.

[0020]

The active ester equivalent (g/eq) of the polyfunctional vinyl aromatic copolymer is preferably 150 to 6000, more preferably 200 to 5000, even more preferably 250 to 4000, particularly preferably 250 to 3000.

The vinyl equivalent (g/eq) of the polyfunctional vinyl aromatic copolymer is preferably 200 to 5000, more preferably 250 to 4000, even more preferably 300 to 3000, particularly 350 to 1500.

[0021]

The number-average molecular weight of the polyfunctional vinyl aromatic copolymer (Mn: number-average molecular weight based on polystyrene standards as measured by gel permeation chromatography) is preferably 300 to 100,000, more preferably 400 to 50,000, even more preferably 500 to 10,000. If the Mn is less than 300, the amount of a monofunctional copolymer component contained in the polyfunctional vinyl aromatic copolymer increases, and therefore the heat resistance of a cured product tends to deteriorate. On the other hand, if the Mn exceeds 10,000, gel is likely to be generated, and therefore molding processability tends to

deteriorate due to an increase in viscosity.

The value of molecular weight distribution (Mw/Mn) represented as a ratio between a weight-average molecular weight (Mw: weight-average molecular weight based on polystyrene standards as measured by gel permeation chromatography) and Mn is 100.0 or less, preferably 50.0 or less, more preferably 1.5 to 30.0, most preferably 2.0 to 20.0. If the Mw/Mn exceeds 100.0, processing characteristics of the polyfunctional vinyl aromatic copolymer tends to deteriorate and gel tends to be generated.

[0022]

The polyfunctional vinyl aromatic copolymer is soluble in a solvent. The polyfunctional vinyl aromatic copolymer is soluble particularly in an organic solvent, for example, toluene, xylene, tetrahydrofuran, dichloroethane or chloroform, but is preferably soluble in all of these solvents. In order to allow the copolymer to be solvent-soluble and polyfunctional, the copolymer needs to have an appropriate degree of cross-linking such that some of vinyl groups of divinylbenzene remain without being cross-linked. The term "solvent-soluble" used herein means that 5 g or more, more preferably 30 g or more, particularly preferably 50 g or more of the polyfunctional vinyl aromatic copolymer is dissolved in 100 g of the solvent.

[0023]

Hereinbelow, a method for producing a polyfunctional vinyl aromatic copolymer of the present invention will be described.

The method for producing a polyfunctional vinyl aromatic copolymer of the present invention is a method including polymerizing a vinyl aromatic compound (a), a vinyl aromatic compound (b) represented by the formula (1) and a monovinyl aromatic compound (c) at a temperature of -20 to 120°C in the presence of a Lewis acid catalyst using the divinyl aromatic compound (a), the vinyl aromatic compound (b) represented by the formula (1) and the monovinyl aromatic compound (c) in an

amount of 2 mol% or more and less than 95 mol%, an amount of 2 mol% or more and less than 93 mol% and an amount of 5 mol% or more and less than 96 mol%, respectively, relative to the sum total of (a), (b) and (c).

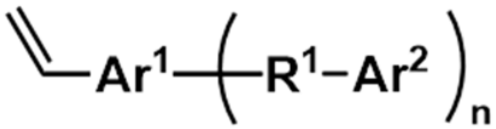
[0024]

The divinyl aromatic compound (a) plays a role of the role of forming a branched structure to achieve polyfunctionality and also plays a role as a cross-linking component for exhibiting heat resistance during thermal curing of the obtained polyfunctional vinyl aromatic copolymer.

The divinyl aromatic compound (a) is not limited as long as it is an aromatic compound having two vinyl groups, but is preferably, for example, divinylbenzene (including position isomers or mixtures of two or more of them), divinyl naphthalene (including position isomers or mixtures of two or more of them), or divinyl biphenyl (including position isomers or mixtures of two or more of them). Further, these may be used singly or in combination of two or more of them. From the viewpoint of molding processability, more preferred is divinylbenzene (an m-isomer, a p-isomer, or a mixture of these position isomers).

[0025]

The ester group-containing vinyl aromatic compound (b) represented by the formula (1) plays the role of improving mechanical properties by increasing the cross-linking density due to a reaction of an active ester group with an epoxy group during thermal curing of the obtained polyfunctional vinyl aromatic copolymer together with an epoxy resin.



(1)

The ester group-containing vinyl aromatic compounds (b) represented by the formula (1) each independently an aromatic ring group with a benzene ring or a

naphthalene ring, and the aromatic ring in each or either of Ar1 and Ar2 contains an ester group of Ar-O-C(=O)-R6 or Ar-C(=O)-O-R7 as a substituent group. R6 represents a hydrocarbon group having 1 to 15 carbon atoms. From the viewpoint of realizing a resin composition excellent in curing reaction property with an epoxy resin, the number of carbon atoms in the hydrocarbon group is in a range of 1 to 15, preferred is an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 14 carbon atoms, and more preferred is an alkyl group having 1 to 3 carbon atoms or an aryl group having 6 to 10 carbon atoms. R7 is an aryl group having 6 to 14 carbon atoms, preferably an aryl group having 6 to 10 carbon atoms.

Ar1 or Ar2 may have an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryl group having 6 to 11 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, an aryloxy group having 6 to 11 carbon atoms, or an aralkyloxy group having 7 to 12 carbon atoms, as a substituent group.

R1 is a direct bond, or a divalent group selected from the group consisting of a hydrocarbon group having 1 to 20 carbon atoms, -CO-, -O-, -S-, -SO2- and -C(CF3)2-.

n is 0 or 1.

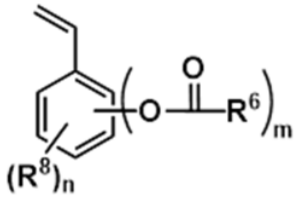
[0026]

Examples of the vinyl aromatic compound (b) represented by the formula (1) include 4-acetoxystyrene, 3-acetoxystyrene, 3,4-diacetoxystyrene, monoacetoxymonovinylnaphthalene, diacetoxymonovinylnaphthalene, 4-vinylphenylbenzoate, 4-acetoxy-4'-vinylbiphenyl, 4-vinylphenyl naphthalenecarboxylate, 3-vinylphenyl naphthalenecarboxylate, 4-vinylphenyl antracenecarboxylate, 3-vinylphenyl antracenecarboxylate, phenyl 4-ethenylbenzoate, and phenyl 4-vinylnaphthalenecarboxylate.

[0027]

In particular, an ester group-containing styrene represented by the following

formula (1) is preferred.



(1a)

In the formula (1a), R6 represents a hydrocarbon group having 1 to 15 carbon atoms, and R4 is an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryl group having 6 to 11 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, an aryloxy group having 6 to 11 carbon atoms, or an aralkyloxy group having 7 to 12 carbon atoms. m represents 1 to 3, and n represents 0 to 3.

[0028]

The monovinyl aromatic compound is a monovinyl aromatic compound (c) other than an ester group-containing vinyl aromatic compound represented by the formula (1). The monovinyl aromatic compound plays the role of imparting low-dielectric properties and thermal oxidative deterioration resistance to the polyfunctional vinyl aromatic copolymer, and plays the role of introducing a vinyl group into the terminal of the polyfunctional vinyl aromatic copolymer.

[0029]

The monovinyl aromatic compound (c) is not limited as long as it is an aromatic compound having one vinyl group, and examples thereof include: vinyl aromatic compounds such as styrene, vinyl naphthalene and vinyl biphenyl; and nuclear-alkylated vinyl aromatic compounds such as o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylvinylbenzene, m-ethylvinylbenzene, and p-ethylvinylbenzene. These may be used singly or in combination of two or more of them.

Preferred is styrene because it prevents gelation of the polyfunctional vinyl

aromatic copolymer and is highly effective at improving solvent solubility and processability, inexpensive, and easily available. From the viewpoint of improving the effects of solvent solubility, processability and dielectric properties, preferred are ethylvinylbenzene (including position isomers or mixtures of two or more of them), ethylvinyl biphenyl (including position isomers or mixtures of two or more of them), and ethylvinyl naphthalene (including position isomers or mixtures of two or more of them). From the viewpoint of dielectric properties and cost, more preferred are styrene and ethylvinylbenzene (an m-isomer, a p-isomer, or a mixture of these position isomers).

[0030]

In addition to the divinyl aromatic compound (a), the ester group-containing vinyl aromatic compound (b) represented by the above formula (1), and the monovinyl aromatic compound (c), a different monomer component (d) such as a trivinyl aromatic compound, a trivinyl aliphatic compound, a divinyl aliphatic compound or a monovinyl aliphatic compound may be used to introduce a structural unit derived from the different component (d) into the polyfunctional vinyl aromatic copolymer as long as the effect of the present invention is not impaired.

[0031]

Examples of the different monomer component (d) include 1,3,5-trivinylbenzene, 1,3,5-trivinylnaphthalene, 1,2,4-trivinylcyclohexane, ethylene glycol diacrylate, butadiene, 1,4-butanediol divinyl ether, cyclohexane dimethanol divinyl ether, diethylene glycol divinyl ether, and triallyl isocyanurate. These may be used singly or in combination of two or more of them.

The mole fraction of the different monomer component (d) relative to the sum total of all the monomer components (a), (b), (c), and (d) is preferably less than 30 mol%. That is, the mole fraction of a repeating unit derived from the different monomer component (d) is preferably less than 30 mol% relative to the sum total of

structural units derived from all the monomer components (a), (b), (c), and (d) constituting the copolymer.

[0032]

If necessary, a vinyl-based compound (e) containing a hydroxyl group, such as hydroxyethyl (meth)acrylate or hydroxypropyl (meth)acrylate may be used as a different monomer to introduce a structural unit derived from (e) into the polyfunctional vinyl aromatic copolymer.

The vinyl-based compound (e) containing a hydroxyl group is contained in an amount equal to a mole fraction preferably of less than 10 mol%, more preferably of less than 5 mol% relative to the sum total of all monomer components (a), (b), (c), (d) and (e). That is, the mole fraction of the structural unit (e) derived from the vinyl-based compound (e) containing a hydroxyl group, relative to the sum total of the structural units in the polyfunctional vinyl aromatic copolymer, is preferably less than 10 mol%.

[0033]

For the proportions of the essential monomer components (a), (b) and (c), the divinyl aromatic compound (a), the ester group-containing vinyl aromatic compound (b) represented by the formula (1), and the monovinyl aromatic compounds (c) are used in an amount of 2 mol% or more and less than 95 mol%, an amount of 2 mol% or more and less than 93 mol% and a combined amount of 5 mol% or more and less than 96 mol%, respectively, relative to the sum total of (a), (b) and (c), and these monomer components (a), (b) and (c) are polymerized at a temperature of -20 to 120°C.

[0034]

The amount of the divinyl aromatic compound (a) to be added is preferably 5 to 80 mol%, more preferably 7 to 70 mol%, even more preferably 10 to 60 mol%.

The amount of the ester group-containing vinyl aromatic compound (b)

represented by the formula (1) to be added is preferably 2 to 80 mol%, more preferably 5 to 70 mol%, even more preferably 5 to 60 mol%.

The total amount of the monovinyl aromatic compound (c) to be added is preferably 5 to 90 mol%, more preferably 10 to 80 mol%, particularly preferably 15 to 70 mol%.

[0035]

The Lewis acid catalyst (f) is a compound composed of a metallic ion (acid) and a ligand (base), and such a compound can be used without limitation as long as it can accept an electron pair. Among such compounds, from the viewpoint of thermal decomposition resistance of the polyfunctional vinyl aromatic copolymer to be obtained, preferred are metal fluorides or complexes thereof, and particularly preferred are fluorides of di- to hexa-valent metals such as B, Al, Ga, In, Si, Ge, Sn, Pb, Sb, Bi, Ti, W, Zn, Fe, and V or complexes thereof. These catalysts may be used singly or in combination of two or more of them. From the viewpoint of control of the molecular weight and molecular weight distribution of the polyfunctional vinyl aromatic copolymer to be obtained and polymerization activity, an ether complex of boron trifluoride is most preferably used. An ether of the ether complex is herein diethyl ether, dimethyl ether, or the like.

The amount of the Lewis acid catalyst (f) to be used is preferably 0.001 to 100 moles, more preferably 0.01 to 50 moles per 100 moles of the total of all the monomer components. Most preferred is 0.1 to 20 moles. If the amount of the Lewis acid catalyst (f) exceeds 100 moles, control of the molecular weight distribution is difficult due to too high a polymerization rate. If the amount of the Lewis acid catalyst (f) to be used is less than 0.001 mol, cost increases and industrial implementation becomes difficult due to too low a polymerization rate.

[0036]

In the method for producing a polyfunctional vinyl aromatic copolymer of the

present invention, at least one Lewis base compound may be used as a promoter (g). Specific examples of the Lewis base compound include ester-based compounds such as propyl acetate, thioester-based compounds such as methylmercaptopropionic acid, ketone-based compounds such as methyl ethyl ketone, amine-based compounds such as methylamine, ether-based compounds such as diethyl ether, thioether-based compounds such as diethyl sulfide, and phosphine-based compounds such as tripropyl phosphine.

Among these, at least one compound selected from the group consisting of ester-based compounds, ketone-based compounds and ether-based compounds is preferred from the viewpoint of synergistically acting with the Lewis acid catalyst (f) to make it possible to easily control the polymerization rate and the molecular weight distribution of the polymer. These Lewis base compounds may be used singly or in combination of two or more of them.

[0037]

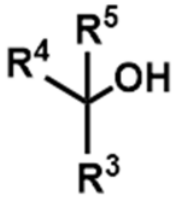
The Lewis base compound coordinates to the Lewis acid catalyst (f) as a counter anion during a polymerization reaction to control interaction between a carbocation as an active species and the counter anion, thereby adjusting the relative frequency of reactions with the monomers (a), (b) and (c) that also function as chain transfer agents. Usually, addition of a Lewis base compound enhances interaction between a carbocation as an active species and a counter anion, so that excessive reactions of the monomers (a), (b) and (c) are suppressed, a chain transfer reaction after the insertion reaction of the monomers (a), (b) and (c) is allowed to easily occur, and it becomes easy to control the molecular weight.

[0038]

In addition to a Lewis base compound, a compound containing a hydroxyl group is regarded as a promoter. It is considered that during a polymerization reaction, the promoter containing a hydroxyl group reacts with the Lewis acid

catalyst (f) to form a carbocation as an active species, which reacts with vinyl groups of the monomers (a), (b) and (c), so that the polymerization reaction proceeds. The promoter containing a hydroxyl group may be used singly, or used in combination with a Lewis base compound.

Specific examples of the promoter containing a hydroxyl group include an alcohol-based compound represented by the following formula (2), examples of which include aromatic compounds such as 1-phenylethanol, 2-phenyl-2-propanol and 2-propanol, and hydrocarbon compounds such as tert-butyl alcohol.



(2)

wherein R3 and R4 are each independently represent an alkyl group having 1 to 6 carbon atoms, or an aromatic hydrocarbon group having 6 to 30 carbon atoms. R5 represents hydrogen, an alkyl group having 1 to 6 carbon atoms, or an aromatic hydrocarbon group having 6 to 30 carbon atoms.

Among these, at least one compound selected from the group consisting of aromatic compounds is preferably used from the viewpoint of synergistically acting with the Lewis acid catalyst (f) to make it possible to easily control the polymerization rate and the molecular weight distribution of the polymer. These hydroxyl group-containing promoters may be used singly or in combination of two or more of them.

[0039]

When a Lewis base compound is used, the amount of the promoter (g) is preferably 0.1 to 1000 moles, more preferably 1.0 to 500 moles, particularly preferably 10 to 200 moles per 100 moles of the total of all the monomer components. When a promoter containing a hydroxyl group is used, the amount of

the promoter (g) is preferably 0.1 to 1000 moles, more preferably 0.5 to 500 moles, particularly preferably 1 to 200 moles per 100 moles of the total of all the monomer components.

When the amount of the hydroxyl group-containing promoter is within the above range, an appropriate polymerization rate is maintained and, at the same time, reaction selectivity between monomers is improved so that a polyfunctional vinyl aromatic copolymer is obtained which is excellent in productivity and has excellent molding processability due to prevention of an excessive increase or decrease in molecular weight.

[0040]

In the polymerization reaction, a copolymer is obtained by subjecting a polymerization starting material containing a mixture of the monomers, for example, to cationic copolymerization at a temperature of -20 to 120°C.

[0041]

If desired, a solvent may be added. As a solvent, preferred is an organic solvent which is a compound that does not essentially inhibit cationic polymerization, dissolves the Lewis acid catalyst (f), the promoter (g), the monomer components, and the polyfunctional vinyl aromatic copolymer to be generated to form a homogeneous solution, and has a permittivity of 2 to 15, and such organic solvents may be used singly or in combination of two or more of them. If the permittivity of the solvent is less than 2, a broad molecular weight distribution is disadvantageously obtained, and if the permittivity of the solvent exceeds 15, the polymerization rate reduces.

From the viewpoint of a balance between polymerization activity and solubility, the organic solvent is particularly preferably toluene, xylene, n-hexane, cyclohexane, methylcyclohexane or ethylcyclohexane. In consideration of the viscosity of a polymerization solution to be obtained and ease of heat removal, the

amount of the solvent to be used is determined in such a manner that the concentration of the copolymer in the polymerization solution at the end of polymerization is 1 to 90 wt%, preferably 10 to 80 wt%, particularly preferably 20 to 70 wt%. If the concentration is less than 1 wt%, low polymerization efficiency leads to an increase in cost, and if the concentration exceeds 90 wt%, the molecular weight and molecular weight distribution of the polyfunctional vinyl aromatic copolymer to be generated increase so that molding processability deteriorates.

[0042]

When the polyfunctional vinyl aromatic copolymer is produced, the monomers (a), (b), and (c) need to be polymerized at a temperature of -20 to 120°C. Preferably, the temperature is 0 to 110°C. Particularly preferably, the temperature is 30 to 90°C. If the polymerization temperature exceeds 120°C, reaction selectivity reduces so that problems such as an increase in molecular weight distribution and generation of gel occur. If the polymerization is performed at a temperature of lower than -20°C, catalyst activity significantly reduces, which creates a need to add a large amount of catalyst.

A method for collecting the polyfunctional vinyl aromatic copolymer after termination of the polymerization reaction is not limited and may be, for example, a method usually used, such as heating concentration, steam stripping, or precipitation in a poor solvent.

[0043]

Hereinbelow, a curable resin composition of the present invention will be described.

The curable resin composition of the present invention contains the polyfunctional vinyl aromatic copolymer of the present invention (including a polyfunctional vinyl aromatic copolymer obtained by the production method of the present invention) and a radical polymerization initiator (h) (also referred to as a

radical polymerization catalyst). The radical polymerization initiator can promote a cross-linking reaction of an unsaturated group, and can efficiently adjust a curing time and a curing temperature.

[0044]

As the radical polymerization initiator (h), a publicly-known substance is used. Typical examples of such a substance include, but are not limited to, peroxides such as benzoyl peroxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, di-t-butyl peroxide, t-butyl cumyl peroxide, α,α'-bis(t-butylperoxy-m-isopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, dicumyl peroxide, di-t-butylperoxy isophthalate, t-butylperoxy benzoate, 2,2-bis(t-butylperoxy)butane, 2,2-bis(t-butylperoxy)octane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, di(trimethylsilyl) peroxide, and trimethylsilyl triphenylsilyl peroxide. Although not a peroxide, 2,3-dimethyl-2,3-diphenylbutane can also be used as a radical polymerization initiator (h). However, the radical polymerization initiator (h) is not limited to these examples. Among these, α,α'-bis(t-butylperoxy-m-isopropyl)benzene is preferably used. The reaction start temperature of α,α'-bis(t-butylperoxy-m-isopropyl)benzene is relatively high. Therefore, it is possible to prevent promotion of a curing reaction at the time when curing does not need to occur, such as during prepreg drying, thereby preventing deterioration of storage stability of the curable resin composition of the present invention. Further, α,α'-bis(t-butylperoxy-m-isopropyl)benzene does not volatilize during prepreg drying or storage due to its low volatility and therefore has good stability. As the radical polymerization initiator (h), only one type of radical polymerization initiator may be used or two or more types of radical polymerization initiators may be used in combination.

The amount of the radical polymerization initiator (h) to be added is preferably 0.01 to 10 parts by weight, more preferably 0.1 to 8 parts by weight per

100 parts by weight of the polyfunctional vinyl aromatic copolymer. When the amount is within such a range, a curing reaction successfully proceeds without being inhibited.

[0045]

In addition, the curable resin composition of the present invention is also a resin composition containing the polyfunctional vinyl aromatic copolymer of the present invention, and an epoxy resin.

[0046]

The epoxy resin preferably has two or more epoxy groups in the molecule, and examples thereof include various epoxy resins such as a bisphenol A-type epoxy resin, a bisphenol F-type epoxy resin, a bisphenol S-type epoxy resin, a bisphenol AF-type epoxy resin, a bisphenol Z-type epoxy resin, a bisphenol fluorene-type epoxy resin, a diphenyl sulfide-type epoxy resin, a diphenyl ether-type epoxy resin, a naphthalene-type epoxy resin, a hydroquinone-type epoxy resin, a resorcinol-type epoxy resin, a phenol novolac-type epoxy, cresol novolac-type epoxy resin, an alkyl novolac-type epoxy resin, a styrenated phenol novolac-type epoxy resin, a bisphenol novolac-type epoxy resin, a naphthol novolac-type epoxy resin, a phenol aralkyl-type epoxy resin, a β-naphthol aralkyl-type epoxy resin, a naphthalene diol aralkyl epoxy resin, an α-naphthol aralkyl-type epoxy resin, a biphenyl aralkyl phenol-type epoxy resin, a biphenyl-type epoxy resin, a triphenylmethane-type epoxy resin, a dicyclopentadiene-type epoxy resin, an alkylene glycol-type epoxy resin, and an aliphatic cyclic epoxy resin.

[0047]

The resin composition containing the polyfunctional vinyl aromatic copolymer of the present invention and an epoxy resin may further contain a radical polymerization initiator for the purpose of promoting a cross-linking reaction of an unsaturated group. Examples of the radical polymerization initiator include the

above substances.

[0048]

The resin composition containing the polyfunctional vinyl aromatic copolymer of the present invention and an epoxy resin may further contain an organic base. When an organic base is contained, a curing reaction with an epoxy group can be promoted, and a curing time and a curing temperature can be efficiently adjusted. As the organic base, at least one selected from amine-based curing accelerator heretofore known as curing accelerators for epoxy resin, organophosphorus-based curing accelerators, and imidazole-based curing accelerators is preferably used.

[0049]

When the resin composition containing the polyfunctional vinyl aromatic copolymer of the present invention and an epoxy resin contains a radical polymerization initiator, the amount of the radical polymerization initiator to be added is preferably in a range of 0.01 to 10 parts by weight, more preferably in a range of 0.05 to 8 parts by weight per 100 parts by weight of resin components in the resin composition.

When the resin composition containing the polyfunctional vinyl aromatic copolymer of the present invention and an epoxy resin contains an organic base, the amount of the organic base to be added is preferably in a range of 0.01 to 10 parts by weight, more preferably in a range of 0.1 to 8 parts by weight per 100 parts by weight of resin components in the resin composition.

[0050]

To the resin composition containing the polyfunctional vinyl aromatic copolymer of the present invention and an epoxy resin, a curing agent for epoxy resin may be added in addition to the polyfunctional vinyl aromatic copolymer of the present invention. The curing agent for epoxy resin is not particularly limited. All

substances commonly known as epoxy resin curing agents may be used. Examples of the epoxy resin curing agent preferred from the viewpoint of enhancing heat resistance include phenol-based curing agents, amide-based curing agents, imidazoles, and active ester-based curing agents. These curing agents may be used singly or in combination of two or more of them.

[0051]

Examples of the epoxy resin curing agent preferred from the viewpoint of improving low permittivity and low dielectric dissipation factor include active ester-based curing agents. For example, 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 are preferred, and among them, phenol esters obtained by reacting a carboxylic acid compound with an aromatic compound having a phenolic hydroxyl group are more preferred. Specific 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.

Examples of the aromatic compound having a phenolic hydroxyl group include catechol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, dihydroxybenzophenone, trihydroxybenzophenone, tetrahydroxybenzophenone, phloroglucin, benzene triol, benzenetriol, dicyclopentadienyldiphenol, and phenol novolac.

[0052]

To the curable resin composition, a known curable reactive resin or thermoplastic resin may be further added. The curable reactive resin includes a thermosetting resin, as well as a resin or compound that is copolymerized with the polyfunctional vinyl aromatic copolymer to form a cured resin. Examples thereof include vinyl ester resins, polyvinyl benzyl resins, unsaturated polyester resins,

curable vinyl resins, curable polyphenylene ether-based resins, maleimide resins, polycyanate resins, phenol resins, and one or more types of vinyl compounds having at least one polymerizable unsaturated hydrocarbon group in a molecule.

Examples of the thermoplastic resin include polystyrene, polyphenylene, ether resins, polyether imide resins, polyether sulfone resins, PPS resins, polycyclopentadiene resins, polycycloolefin resins, phenoxy resins, known thermoplastic elastomers such as styrene-ethylene-propylene copolymers, styrene-ethylene-butylene copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, hydrogenated styrene-butadiene copolymers, and hydrogenated styrene-isoprene copolymers, and rubbers such as polybutadiene and polyisoprene.

[0053]

From the viewpoint of dielectric properties, heat resistance, and adhesiveness required of the curable resin composition and compatibility with the polyfunctional vinyl aromatic copolymer, preferred examples of the curable reactive resin include polyvinyl benzyl resins, curable vinyl resins, curable polyphenylene ether-based resins, and one or more types of vinyl compounds having at least one polymerizable unsaturated hydrocarbon group in a molecule and preferred examples of the thermoplastic resin include polystyrene, polyphenylene ether resins, styrene-ethylene-propylene copolymers, styrene-ethylene-butylene copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, hydrogenated styrene-butadiene copolymers, and hydrogenated styrene-isoprene copolymers. More preferred examples of the curable reactive resin include polyvinyl benzyl resins, curable polyphenylene ether-based resins, epoxy resins, and one or more types of vinyl compounds having at least one polymerizable unsaturated hydrocarbon group in a molecule, and more preferred examples of the thermoplastic resin (i) include polyphenylene ether resins and hydrogenated styrene-butadiene copolymers.

[0054]

When the curable reactive resin is a curable polyphenylene ether-based resin, more preferred is a modified polyphenylene ether compound having a curable terminal functional group. Even more preferred is a modified polyphenylene ether compound having an unsaturated hydrocarbon group. Still even more preferred is a modified polyphenylene ether compound terminally modified with a substituent group having a carbon-carbon unsaturated double bond. Most preferred is a modified polyphenylene ether compound having a curable terminal functional group such that the substituent group having a carbon-carbon unsaturated double bond is a substituent group selected from the group consisting of a vinyl benzyl group, a vinyl group, an acrylate group, and a methacrylate group.

The average number of unsaturated hydrocarbon groups (number of terminal functional groups) in one molecule of the modified polyphenylene ether compound having an unsaturated hydrocarbon group at its terminal is not limited. From the viewpoint of the heat resistance of a cured product and a balance between the storage stability and flowability of the curable resin composition, the average number is preferably 1 to 5, more preferably 1 to 3, even more preferably 1.5 to 3.

[0055]

The Mn of the curable polyphenylene ether-based resin is not limited but is preferably 500 to 7000, more preferably 800 to 5000, most preferably 1000 to 3000. It should be noted that the Mn is herein measured by a general molecular weight measurement method and may specifically be a value measured by gel permeation chromatography (GPC).

When the Mn of the curable polyphenylene ether-based resin is within such a range, a cured product of the obtained curable resin composition has higher toughness and moldability. This is because the curable polyphenylene ether-based resin whose number-average molecular weight is within such a range has a relatively low molecular weight, and therefore flowability is improved while toughness is

maintained. When a common polyphenylene ether having such a low molecular weight is used, the heat resistance and toughness of a cured product tend to deteriorate. However, the curable polyphenylene ether-based resin has a polymerizable unsaturated double bond at its terminal, and therefore when the curable polyphenylene ether-based resin is copolymerized with or cured together with a vinyl-based curable resin such as the copolymer of the present invention, cross-linking of both the resins appropriately proceeds so that a cured product is obtained which has sufficiently high heat resistance and toughness. Therefore, a cured product of the obtained curable resin composition is excellent in both heat resistance and toughness.

[0056]

When the curable reactive resin is at least one vinyl compound (id) having at least one polymerizable unsaturated hydrocarbon group in the molecule, the vinyl compound (id) is not particularly limited. That is, (id) is not limited as long as it can be reacted with the polyfunctional vinyl aromatic copolymer of the present invention to form cross-links to achieve curing. More preferably, the polymerizable unsaturated hydrocarbon group is a carbon-carbon unsaturated double bond. More preferred is a compound having two or more carbon-carbon unsaturated double bonds in its molecule.

[0057]

The weight-average molecular weight (Mw) of the vinyl compound as a curable reactive resin is preferably 100 to 5,000, more preferably 100 to 4,000, even more preferably 100 to 3,000. If the Mw is less than 100, there is a fear that (id) is likely to volatilize from a blended component system of the curable resin composition. On the other hand, if the Mw exceeds 5,000, there is a fear that the viscosity of a varnish of the curable resin composition and melt viscosity during heat molding are too high. Therefore, when the Mw of (id) is within such a range, a

curable resin composition is obtained which provides a cured product having excellent heat resistance. The reason for this is considered to be that cross-links can appropriately be formed by a reaction between the polyfunctional vinyl aromatic copolymer and (id). The Mw is herein measured by a general molecular weight measurement method and may specifically be a value measured by gel permeation chromatography (GPC).

[0058]

The average number of carbon-carbon unsaturated double bonds (number of terminal double bonds) per molecule of the vinyl compound as a curable reactive resin depends on the Mw, but is, for example, preferably 1 to 20, more preferably 2 to 18. If the number of terminal double bonds is too small, a cured product having sufficient heat resistance is less likely to be obtained. If the number of terminal double bonds is too large, reactivity is too high so that problems such as deterioration of storage stability of the curable resin composition and deterioration of flowability of the curable resin composition may occur.

[0059]

Examples of the vinyl compound (id) as a curable reactive resin include a trialkenyl isocyanurate compound such as triallyl isocyanurate (TAIC), a polyfunctional methacrylate compound having two or more methacrylic groups in its molecule, a polyfunctional acrylate compound having two or more acrylic groups in its molecule, a vinyl compound (polyfunctional vinyl compound) having two or more vinyl groups in its molecule, such as polybutadiene, styrene having a vinylbenzyl group in its molecule, and a vinylbenzyl compound such as divinylbenzene. Among these, preferred is one having two or more carbon-carbon double bonds in its molecule. Specific examples thereof include a trialkenyl isocyanurate compound, a polyfunctional acrylate compound, a polyfunctional methacrylate compound, a polyfunctional vinyl compound, and a divinylbenzene compound. It is considered

that when such a compound is used, cross-links are more appropriately formed by a curing reaction so that a cured product of the curable resin composition can have higher heat resistance. These may be used singly or in combination of two or more of them. A compound having one carbon-carbon unsaturated double bond in its molecule may be used in combination therewith. The compound having one carbon-carbon unsaturated double bond in its molecule may be, for example, a compound (monovinyl compound) having one vinyl group in its molecule.

[0060]

The content of the polyfunctional vinyl aromatic copolymer is preferably 30 to 90 parts by mass, more preferably 50 to 90 parts by mass per 100 parts by mass of the total of the polyfunctional vinyl aromatic copolymer and the vinyl compound (id) as a curable reactive resin. The content of the vinyl compound (id) as a curable reactive resin is preferably 10 to 70 parts by mass, more preferably 10 to 50 parts by mass per 100 parts by mass of the total of the polyfunctional vinyl aromatic copolymer and (id). That is, the content ratio by mass between the polyfunctional vinyl aromatic copolymer and the vinyl compound (id) as a curable reactive resin is preferably 90:10 to 30:70, more preferably 90:10 to 50:50. When the contents of the polyfunctional vinyl aromatic copolymer and (id) satisfy the above ratio, a curable resin composition is obtained which provides a cured product having more excellent heat resistance and flame retardancy. The reason for this is considered to be that a curing reaction between the polyfunctional vinyl aromatic copolymer and the vinyl compound (id) as a curable reactive resin appropriately proceeds.

[0061]

The curable resin composition of the present invention may contain a known flame retardant (k). The flame retardant (k) can further enhance the flame retardancy of a cured product of the curable resin composition. The flame retardant (k) is not limited. Specifically, in fields where halogen-based flame retardants such

as bromine-based flame retardants are used, preferred examples thereof include ethylenedipentabromobenzene, ethylenebistetrabromoimide, decabromodiphenyloxide, and tetradecabromodiphenoxybenzene which have a melting point of 300°C or higher. It is considered that using such a halogen-based flame retardant can prevent halogen elimination at high temperatures, thereby preventing deterioration of heat resistance. In fields requiring halogen-free flame retardants, examples of such flame retardants include phosphoric acid ester-based flame retardants, phosphazene-based flame retardants, and phosphinic acid salt-based flame retardants. Specific examples of the phosphoric acid ester-based flame retardants include condensed phosphoric acid esters such as dixylenyl phosphate and the like. Specific examples of the phosphazene-based flame retardants include phenoxyphosphazenes. Specific examples of the phosphinic acid salt-based flame retardants include phosphonic acid metal salts such as aluminum dialkyl phosphinates. These flame retardants exemplified above may be used singly or in combination of two or more of them.

[0062]

The curable resin composition of the present invention may contain a known filler (l). The filler (l) is not limited and may be, for example, one added to enhance the heat resistance and flame retardancy of a cured product of the curable resin composition. Addition of the filler (l) can further enhance heat resistance and flame retardancy. Specific examples of the filler (m) include silica such as spherical silica, metal oxides such as alumina, titanium oxide, and mica, metal hydroxides such as aluminum hydroxide and magnesium hydroxide, talc, aluminum borate, barium sulfate, and calcium carbonate. Among these, preferred are silica, mica, and talc, and more preferred is spherical silica. These may be used singly or in combination of two or more of them. The filler may be used as it is or may be used after subjected to surface treatment with an epoxy silane- or aminosilane-type silane

coupling agent. From the viewpoint of reactivity with the radical polymerization initiator (h), the silane coupling agent is preferably a vinylsilane-, methacryloxysilane-, acryloxysilane-, or styrylsilane-type silane coupling agent. This makes it possible to increase adhesive strength with metallic foil or interlayer adhesive strength between resins. The silane coupling agent may be added by an integral blending method instead of a method in which the filler (l) is previously surface-treated therewith.

The content of the filler (l) is preferably 10 to 200 parts by mass, preferably 30 to 150 parts by mass per 100 parts by mass of the total of an organic component such as monomers and the flame retardant.

[0063]

The curable resin composition of the present invention may further contain an additive other than the flame retardant and the filler. Examples of such an additive include a defoaming agent such as a silicone-based defoaming agent or an acrylic acid ester-based defoaming agent, a heat stabilizer, an antistatic agent, a UV absorber, a dye or a pigment, a lubricant, and a dispersant such as a wetting and dispersing additive.

[0064]

When used for prepreg production, the curable resin composition of the present invention can be prepared in the form of a varnish to be used as a resin varnish for the purpose of impregnating a base material (fibrous base material) for forming prepregs therewith or providing a circuit board material for forming a circuit board.

The resin varnish contains the polyfunctional vinyl aromatic copolymer, the radical polymerization initiator (h), and a solvent. If desired, the resin varnish may contain one or more of the curable reactive resin, the thermoplastic resin, the flame retardant, the filler, and other additives. This resin varnish is suitable for circuit

boards and therefore can be used as a varnish for circuit board materials. Specific uses of the circuit board materials are printed wiring boards, printed circuit boards, flexible printed wiring boards, build-up wiring boards, and the like.

[0065]

The resin varnish is prepared, for example, in the following manner.

First, components in an organic solvent, such as the polyfunctional vinyl aromatic copolymer and the curable reactive resin (i), are added to and dissolved in the organic solvent. At this time, heat may be applied, if necessary. If necessary, components insoluble in the organic solvent, such as an inorganic filler etc., are then added and dispersed using a ball mill, a bead mill, a planetary mixer, or a roll mill to prepare a curable resin composition in the form of a varnish. The organic solvent used herein is not limited as long as it can dissolve the polyfunctional vinyl aromatic copolymer, (i), etc. and does not inhibit a curing reaction. Examples of such an organic solvent include: ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; esters such as ethyl acetate, propyl acetate, and butyl acetate; polar solvents such as dimethyl acetamide and dimethyl formamide; and aromatic hydrocarbon solvents such as toluene and xylene. These may be used singly or in combination of two or more of them. From the viewpoint of dielectric properties, preferred are aromatic hydrocarbons such as benzene, toluene, and xylene.

When the resin varnish is prepared, the amount of the organic solvent to be used is preferably 5 to 900 wt%, more preferably 10 to 700 wt%, particularly preferably 20 to 500 wt% relative to the amount of the curable resin composition of the present invention taken as 100 wt%. It should be noted that when the curable resin composition of the present invention is an organic solvent solution such as a resin varnish, the amount of the organic solvent is not included in the calculation of the composition.

[0066]

A cured product obtained by curing the curable resin composition of the present invention can be used as a molded product, a laminate, a cast product, an adhesive, a coating, or a film. For example, a cured product of a semiconductor sealing material is a cast product or a molded product, and a cured product for such an intended use can be obtained by a method in which the curable resin composition is cast or molded using a transfer molding machine, an injection molding machine, or the like and is further heated at 80 to 230°C for 0.5 to 10 hours. A cured product of a varnish for circuit boards is a laminate, and such a cured product can be obtained by a method in which a base material such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, alumina fibers, or paper is impregnated with the varnish for circuit boards and dried by heating to obtain prepregs, and the prepregs are stacked with or without a metallic foil such as a copper foil being interposed between them and then molded by hot press.

[0067]

Adding an inorganic high-dielectric powder such as barium titanate or an inorganic magnetic material such as ferrite to the curable resin composition or the resin varnish makes the curable resin composition or the resin varnish more excellent as a material for electronic parts, especially as a material for high-frequency electronic parts.

[0068]

The curable resin composition of the present invention may be bonded to a metallic foil (intended to include a metal sheet; the same applies hereinafter) like a cured composite material which will be described later.

[0069]

Next, the curable composite material of the curable resin composition of the present invention, and cured products thereof will be described. Such a curable composite material is produced by adding a base material to the curable resin

composition of the present invention to increase mechanical strength and enhance dimensional stability.

As the base material, a publicly-known material is used, and examples thereof include cloths and paper such as various glass cloths such as roving cloths, cloths, chopped mats, and surfacing mats, asbestos cloths, metallic fiber cloths and other synthetic or natural inorganic fiber cloths, woven or nonwoven cloths obtained from liquid crystal fibers such as wholly aromatic polyamide fibers, wholly aromatic polyester fibers, or polybenzazole fibers, woven or nonwoven cloths obtained from synthetic fibers such as polyvinyl alcohol fibers, polyester fibers, or acrylic fibers, natural fiber cloths such as cotton cloths, hemp cloths, and felt, carbon fiber cloths, and natural cellulose-based cloths such as craft paper, cotton paper, and paper-glass mixed paper. These may be used singly or in combination of two or more pf them.

The proportion of the base material in the curable composite material is preferably 5 to 90 wt%, more preferably 10 to 80 wt%, even more preferably 20 to 70 wt%. If the proportion of the base material is less than 5 wt%, the composite material after curing is poor in dimensional stability and strength, and if the proportion of the base material is more than 90 wt%, the composite material is disadvantageously poor in dielectric properties.

If necessary, a coupling agent may be used for the curable composite material of the present invention for the purpose of improving adhesion at an interface between the resin and the base material. The coupling agent to be used may be commonly-used one such as a silane coupling agent, a titanate coupling agent, an aluminum-based coupling agent, or a zircoaluminate coupling agent.

[0070]

A method for producing the curable composite material of the present invention may be, for example, a method in which the curable resin composition of the present invention and an optional different component are uniformly dissolved or

dispersed in the above-described solvent such as an aromatic solvent or a ketone-based solvent or a mixed solvent thereof, and a base material is impregnated therewith and then dried. The impregnation is performed by, for example, immersion (dipping) or coating. If necessary, the impregnation may be repeated two or more times, and in this case, a plurality of solutions different in composition or concentration may be used for repeated impregnation to finally achieve a desired resin composition and a desired resin amount.

[0071]

When the curable composite material of the present invention is cured by, for example, heating, a cured composite material is obtained. A method for producing the cured composite material is not limited. For example, when a plurality of layers of the curable composite material are stacked on top of each other, and heat and pressure are applied thereto to bond the layers together while thermally curing the layers, a cured composite material having a desired thickness can be obtained. A cured composite material previously obtained through bonding and curing may be combined with the curable composite material to obtain a cured composite material having a new layer structure. The lamination molding and the curing are usually performed at the same time using a hot press or the like but may be performed independently from each other. Specifically, an uncured or semi-cured composite material previously obtained through lamination molding may be cured by heat treatment or another treatment.

Curing or molding and curing of the curable resin composition or the curable composite material of the present invention can be performed preferably at a temperature of 80 to 300°C and a pressure of 0.1 to 1000 kg/cm^2 for 1 minute to 10 hours, more preferably at a temperature of 150 to 250°C and a pressure of 1 to 500 kg/cm^2 for 1 minute to 5 hours.

[0072]

A laminate of the present invention is constituted from a layer of the cured composite material of the present invention and a layer of metallic foil. Examples of the metallic foil used herein include copper foil and aluminum foil. The thickness thereof is not limited but is 3 to 200 μm, more preferably 3 to 105 μm.

A method for producing the laminate of the present invention may be, for example, a method in which a curable composite material, obtained from the above-described curable resin composition of the present invention and a base material, and a metallic foil are stacked to form a layer structure suitable for intended use, and heat and pressure are applied thereto to bond the layers together while thermally curing the layers. In the laminate using the curable resin composition of the present invention, a cured composite material and a metallic foil are laminated to form any layer structure. The metallic foil can be used as both a top layer and an intermediate layer. The lamination and curing may be repeated two or more times to obtain a multilayer laminate.

An adhesive may be used for bonding with the metallic foil. Examples of the adhesive include, but are not limited to, an epoxy-based adhesive, an acrylic adhesive, a phenol-based adhesive, and a cyanoacrylate-based adhesive.

The lamination molding and the curing can be performed under the same conditions as in production of the cured composite material of the present invention.

[0073]

The curable resin composition of the present invention may be molded into a film shape to provide a film which is one form of the curable resin composition of the present invention. The thickness thereof is not limited but is preferably 3 to 200 μm, more preferably 5 to 105 μm.

A method for producing the film of the present invention is not limited and may be, for example, a method in which the curable resin composition is uniformly dissolved or dispersed in a solvent such as an aromatic solvent or a ketone-based

solvent or a mixed solvent thereof and the resultant is applied onto a resin film such as a PET film and then dried. If necessary, the application may be repeated two or more times, and in this case, a plurality of solutions different in composition or concentration may be used for repeated application to finally achieve a desired resin composition and a desired resin amount.

[0074]

A metallic foil with resin of the present invention is constituted from the curable resin composition of the present invention and a metallic foil. Examples of the metallic foil include copper foil and aluminum foil.

The thickness thereof is not limited but is preferably 3 to 200 μm, more preferably 5 to 105 μm.

A method for producing the metallic foil with resin of the present invention is not limited and may be, for example, a method in which the curable resin composition is uniformly dissolved or dispersed in a solvent such as an aromatic solvent or a ketone-based solvent or a mixed solvent thereof and the resultant is applied onto a metallic foil and then dried. If necessary, the application may be repeated two or more times, and in this case, a plurality of solutions different in composition or concentration may be used for repeated application to finally achieve a desired resin composition and a desired resin amount.

[0075]

The polyfunctional vinyl aromatic copolymer of the present invention may be processed into a molding material, a sheet or a film, and may be used for low-permittivity materials, insulating materials, heat-resistant materials, structural materials and the like which can satisfy properties such as low permittivity, low water absorption, high heat resistance and the like in the fields of, for example, electrical industries, space and aircraft industries, and automobiles. In particular, the polyfunctional vinyl aromatic copolymer of the present invention may be used

for single-sided, double-sided and multi-layered printed boards, flexible printed boards, build-up boards, and the like.

The polyfunctional vinyl aromatic copolymer of the present invention is applicable to semiconductor materials or optical materials, and coating materials, photosensitive materials, adhesives, wastewater treatment agents, heavy metal collection agents, ion-exchange resins, antistatic agents, antioxidants, anti-fogging agents, anti-rust agents, dye preventing agents, bactericides, insect repellents, medical materials, aggregating agents, surfactants, lubricants, binders for solid fuel, conductive property imparting agents, resin modifiers, asphalt modifier plasticizers, and sintering binders.

[0076]

The curable resin composition of the present invention has high dielectric properties (low permittivity and low dielectric dissipation factor) even after severe heat history, provides a cured product having high adhesion reliability even in a severe environment, and has excellent resin fluidity, low expansivity, and excellent ability to form a flat wiring-embedded shape. Therefore, cured molded articles capable of responding miniaturization and thinning that have been strongly demanded in recent years, and free of a molding defect phenomenon such as warp can be provided as dielectric materials, insulating materials, heat-resistant materials, structural materials and the like in the fields of electrical/electronic industries, space and aircraft industries, and the like. Further, due to excellent ability to form a flat wiring-embedded shape and excellent adhesion to a different kind of material, a curable resin composition having high reliability, a cured product, or a material containing the cured product can be realized.

Examples

[0077]

Hereinbelow, the present invention will be described with reference to examples, but the present invention is not limited by these examples. The term "part(s)" in examples refers to part(s) by weight.

It should be noted that physical property measurements in the examples were performed by the following methods.

[0078]

1) Weight-average molecular weight

The weight-average molecular weight was determined by GPC measurement. Specifically, a main body HLC8320GPC (manufactured by Tosoh Corporation) to which columns (TSKgel SuperH-H, SuperH2000, SuperHM-H, and SuperHM-H, all manufactured by Tosoh Corporation) were connected in series was used, and the column temperature was 40°C. As an eluent, tetrahydrofuran (THF) was used, the flow rate was 1 mL/min, and a differential refractive index detector was used as a detector. 20 μL of a measurement sample obtained by dissolving 0.1 g of a solid content in 10 mL of THF, and filtering the solution through a microfilter with a pore size of 0.45 μm was used. Mw was determined on the basis of a calibration curve obtained using standard polystyrene oxides (manufactured by Tosoh Corporation, SE-2, SE-5, SE-8, SE-15, SE-30, SE-70, and SE-150).

2) Structure of polymer

The presence or absence of a structure of the formula (b1) was determined by 13C-NMR and 1H-NMR analyses using a JNM-LA600 nuclear magnetic resonance spectrometer manufactured by JEOL Ltd. As a solvent, chloroform-d1 was used as a solvent, and a resonance line of tetramethylsilane was used as an internal standard.

3) Active ester equivalent

The active ester equivalent was measured by referring to JIS K0070 Standard. Specifically, a sample was dissolved in THF, reacted with a 0.5 mol/L solution of potassium hydroxide in ethanol, and subjected to neutralization titration with 0.5

mol/L hydrochloric acid with phenolphthalein as an indicator to test an ester value.

4) Vinyl equivalent

The vinyl equivalent was measured by referring to JIS K0070 Standard. Specifically, a Wijs solution (iodine monochloride solution) was reacted with a sample, the reaction product was left to stand in a dark place, excess iodine chloride was then reduced to iodine, and an iodine content was titrated with sodium thiosulfate to calculate an iodine value. The iodine value was converted into a vinyl equivalent.

5) Tanδ in dynamic viscoelasticity measurement

A 2 mm-thick molded product of a cured resin was processed into a test piece (60 mm in length and 10 mm in width). The dynamic viscoelasticity was measured at a frequency of 10 Hz and a temperature raising rate of 5°C/min and in a range from 20°C to 250°C using a dynamic viscoelasticity measurement apparatus (DMA7100 manufactured by Hitachi High-Tech Corporation), and a peak temperature at the obtained Tanδ was read. When a plurality of peaks were observed, a temperature at each peak was read.

6) Flexural property of cured product

A 2 mm-thick molded product of a cured resin was processed into a test piece (100 mm in length and 10 mm in width), and a flexural property of the resin test piece was measured using a universal tester equipped with a 1000 N load cell (AGS-X manufactured by Shimadzu Corporation). A flexural modulus and a stress at a break point of the test piece were measured in an environment at a temperature of 23°C and a humidity of 50% RH using a three-point bending jig.

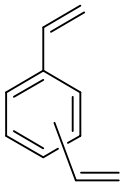
7) Measurement of haze of cured product

A 0.7 mm-thick molded product of a cured resin was processed into 50 mm × 50 mm, and a haze value was measured using a spectrophotometric colorimeter (CM-5 manufactured by Konica Minolta, Inc.

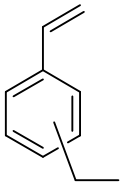
[0079]

Example 1

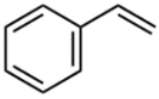
In a 1.0 L reaction container, 0.60 mol (78 g) of divinylbenzene,



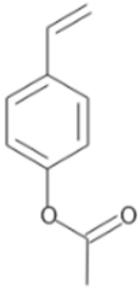
0.35 mol (46 g) of ethylvinylbenzene,



1.75 mol (182 g) of styrene,



0.30 mol (49 g) of 4-acetoxystyrene,



0.12 mol (15 g) of 1-phenylethanol as a promoter, 250 g of toluene, and 7.9 g of a diethyl ether complex of boron trifluoride as a catalyst were placed and subjected to reaction at 40°C for 6 hours. The polymerization reaction was terminated using methanol and an aqueous sodium hydrogen carbonate solution, and an oil layer was then washed with pure water three times and subjected to vacuum devolatilization at 40°C to obtain a copolymer 1.

The copolymer 1 obtained in Example 1 was confirmed by NMR measurement to have a structural unit represented by the formula (b1). The active ester equivalent and the vinyl equivalent were measured, and the results showed that the copolymer 1 obtained in Example 1 had an active ester equivalent of 1015 g/eq. and a vinyl equivalent of 623 g/eq. The IR chart and the GPC chart of the copolymer are shown in Figure 1 and Figure 2, respectively.

[0080]

Example 2

In a 1.0 L reaction container, 0.60 mol (78.1 g) of divinylbenzene, 0.35 mol (46.3 g) of ethylvinylbenzene, 1.75 mol (182.3 g) of styrene, 0.30 mol (48.7 g) of 4-acetoxystyrene, 307 g of propyl acetate, 0.17 g of water, and 8.5 g of a diethyl ether complex of boron trifluoride were placed, and subjected to reaction at 70°C for 8 hours. The polymerization reaction was terminated using methanol and an aqueous sodium hydrogen carbonate solution, and an oil layer was then washed with pure water three times and subjected to vacuum devolatilization at 40°C to obtain a copolymer 2.

[0081]

Examples 3 to 5

The same procedure as in Example 1 was carried out to obtain a copolymer 3, a copolymer 4 and a copolymer 5 according to the loading amounts (parts) of the raw materials as shown in Table 1.

[0082]

Comparative Example 1

Except that 4-acetoxystyrene was not used, the same procedure as in Example 1 was carried out to obtain a copolymer 6 according to the loading amounts (parts) of the raw materials as shown in Table 1.

Various physical properties of the copolymers obtained in Examples 1 to 5

and Comparative Example 1 were measured. Table 1 shows the results.

[0083]

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1
	Copolymer 1	Copolymer 2	Copolymer 3	Copolymer 4	Copolymer 5	Copolymer 6
Divinylbenzene (g)	78	78	64	40	81.9	78
Ethylvinylbenzene (g)	46	46	38	23	48.3	46
Styrene (g)	182	182	-	242	200	220
4-Acetoxystyrene (g)	49	49	252	53	26	-
Diethyl ether complex of boron trifluoride (g)	7.9	8.5	7.9	7.9	7.9	7.9
1-Phenylethanol (g)	15	-	15	15	15	15
Toluene (g)	250	-	250	250	250	250
Propyl acetate (g)	-	307	-	-	-	-
Reaction temperature	40	70	40	40	40	40
Reaction time	6	8	6	6	4	5
Mn	2200	5000	2200	2700	2100	3700
Mw	12900	30800	13500	6900	11200	12900
Mw/Mn	5.9	6.2	6.1	2.6	5.3	3.5
Presence or absence of (b1) structural unit	Present	Present	Present	Present	Present	Absent
Active ester equivalent (g/eq.)	1015	1030	240	1080	2100	-
Vinyl equivalent (g/eq.)	480	500	650	980	540	-

[0084]

Next, Examples for cured products with an epoxy resin will be described, and the components used are as follows.

[Epoxy resin]

Epoxy resin: a mixed product of a bisphenol A-type epoxy resin and a bisphenol F-type epoxy resin (ZX-1059, manufactured by NIPPON STEEL Chemical & Material Co., Ltd., epoxy equivalent 166 g/eq.)

[0085]

[Synthesis Example 1: Active ester curing agent]

In a reaction apparatus equipped with a stirrer, a thermometer, a nitrogen blowing ring, a dropping funnel and a cooling pipe, 165 parts of phenolated dicyclopentadiene (J-DPP-85, manufactured by JFE Chemical Corporation, hydroxyl group equivalent 165), 144 parts of 1 naphthol, 203 parts of isophthaloyl chloride, 10 parts of tetra n-butylammonium bromide, and 1280 parts of toluene were loaded, and dissolved by raising the temperature to 50°C. While the inside of the system was maintained at 60°C or lower, 400 parts of a 20% aqueous sodium hydroxide solution was added dropwise over 3 hours, and the mixture was then continuously stirred at the same temperature for another 4 hours. The reaction mixture was placed still for liquid separation, and the aqueous layer was removed. This procedure was repeated until the pH of the aqueous layer became 7. Thereafter, water was removed by reflux dehydration to obtain an active ester resin in the form of a toluene solution having a non-volatile matter content of 65%. The active ester equivalent calculated from the loading amounts of raw materials was 220 g/eq.

[0086]

[Peroxide]

α,α'-Bis(2-t-butylperoxyisopropyl)benzene (manufactured by NOF Corporation, PERBUTYL P)

[Catalyst]

N,N'-Dimethylaminopyridine (manufactured by Tokyo Chemical Industry Co., Ltd., DMAP)

[0087]

Example 6

23.3 parts of the copolymer obtained in Example 1, 10 parts of the epoxy resin ZX-1059, 13.3 parts of the active ester curing agent obtained in Synthesis Example 1, 0.1 parts of PERBUTYL P as a peroxide, and 0.1 parts of DMAP as a catalyst were mixed, and diluted to a non-volatile matter content of 50% with toluene to obtain a resin composition. Further, the resin composition was applied in a thickness of 150 μm to a PET film, and dried at 130°C for 15 minutes using a drier. The obtained dry powder was pressed for 90 minutes under conditions of vacuum at 0.5 kPa, a heating temperature of 220°C and a pressing pressure of 2 MPa to obtain a 2 mm-thick cured product. A 2 mm spacer was used for thickness adjustment. The dynamic viscoelasticity (Tanδ), the haze value and the mechanical strength (stress at flexural break point) of the cured product were measured. Table 2 shows the results.

[0088]

Examples 7 to 12 and Comparative Examples 2 to 4

The formulations shown in Table 2 were set, and the same procedure as in Example 6 was carried out to obtain a cured product. The dynamic viscoelasticity (Tanδ), the haze value and the mechanical strength (stress at flexural break point) of the cured product were measured. Table 2 shows the results.

[0089]

[Table 2]

	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comparative Example 2	Comparative Example 3	Comparative Example 4
Copolymer 1	23.3	19.2	18.4							
Copolymer 2				19.2						
Copolymer 3					21.7					
Copolymer 4						19.2				
Copolymer 5							28.0			
Copolymer 6								23.3	19.5	16.2
Epoxy resin ZX-1059	10.0	10.0	3.0	21.5	15	10	10	10.0	10.0	10.0
Active ester curing agent	13.3	9.2		28.5		8.9	10.3	13.3	13.3	9.2
4-acetoxystyrene									3.7	3.1
PERBUTYL P	0.1	0.1	0.1	0.5	0.1	0.1	0.1	0.1	0.1	0.1
DMAP	0.1	0.1	0.03		3	0.1	0.1	0.1	0.1	0.1
Tanδ (°C)	122	129	150	134	165	115	125	138/186	135/179	118/175
Haze value (%)	37	39	42	45	35	40	43	90	87	85
Stress at flexural break point (MPa)	84	114	90	100	125	101	110	70	77	80

[0090]

In Examples, a cured product including a resin composition of the polyfunctional vinyl aromatic copolymer of the present invention and an epoxy resin had one Tanδ peak and had a reduced haze value, and therefore it can be seen that through a cross-linking reaction with an epoxy resin, the polyfunctional vinyl aromatic copolymer of the present invention provided a cured product having improved uniformity and reactivity, and improved mechanical strength.

Industrial Applicability

[0091]

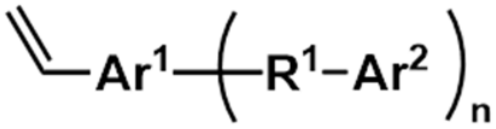
The polyfunctional vinyl aromatic copolymer of the present invention is useful for electrical insulating materials for high-speed communication devices, especially for printed wiring boards.

Claims

[Claim 1]

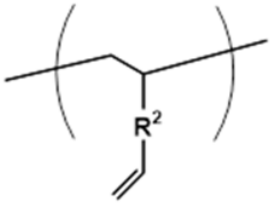
A polyfunctional vinyl aromatic copolymer obtained by using 2 mol% or more and less than 95 mol% of a divinyl aromatic compound (a), 2 mol% or more and less than 93 mol% of an ester group-containing vinyl aromatic compound (b) represented by the following formula (1), and 5 mol% or more and less than 96 mol% of a monovinyl aromatic compound (c),

the copolymer containing a structural unit represented by the following formula (a1) derived from the divinyl aromatic compound (a) and a structural unit represented by the following formula (b1) derived from the ester group-containing vinyl aromatic compound (b), having a number-average molecular weight of 300 to 100,000 and a molecular weight distribution (Mw/Mn), which is represented as a ratio between a weight-average molecular weight and a number-average molecular weight, of 100 or less and being soluble in a solvent:



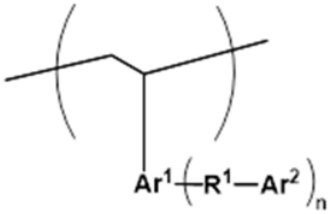
(1)

wherein Ar1 and Ar2 are each independently an aromatic ring group with a benzene ring or a naphthalene ring, and the aromatic ring in each or either of Ar1 and Ar2 contains an ester group having 1 to 15 carbon atoms as a substituent group, and may have an alkyl group having 1 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, an aryl group having 6 to 11 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, an aryloxy group having 6 to 11 carbon atoms, or an aralkyloxy group having 7 to 12 carbon atoms, as a substituent group, R1 is a direct bond, or a divalent group selected from the group consisting of a hydrocarbon group having 1 to 20 carbon atoms, -CO-, -O-, -S-, -SO2- and -C(CF3)2-, and n is 0 or 1,



(a1)

wherein R2 represents an aromatic hydrocarbon group having 6 to 30 carbon atoms,



(b1)

wherein Ar1, Ar2, R1 and n are as defined in the formula (1).

[Claim 2]

The polyfunctional vinyl aromatic copolymer according to claim 1, wherein an active ester equivalent is 150 to 6000 g/eq., and a vinyl equivalent is 200 to 5000 g/eq.

[Claim 3]

A curable resin composition containing the polyfunctional vinyl aromatic copolymer according to claim 1, and a radical polymerization initiator.

[Claim 4]

A resin composition containing the polyfunctional vinyl aromatic copolymer according to claim 1, and an epoxy resin.

[Claim 5]

A curable resin composition containing the polyfunctional vinyl aromatic copolymer according to claim 1, and a curable reactive resin or thermoplastic resin, or a flame retardant or filler.

[Claim 6]

A cured product obtained by curing the curable resin composition according

to any one of claims 3 to 5.

[Claim 7]

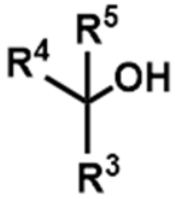
A method for producing the polyfunctional vinyl aromatic copolymer according to claim 1, the method comprising polymerizing a divinyl aromatic compound (a), an ester group-containing vinyl aromatic compound (b) represented by the formula (1) and a monovinyl aromatic compound (c) at a temperature of -20 to 120°C in the presence of a Lewis acid catalyst (f) and a promoter (g) using the divinyl aromatic compound (a), the ester group-containing vinyl aromatic compound (b) represented by the formula (1) and the monovinyl aromatic compound (c) in an amount of 2 mol% or more and less than 95 mol%, an amount of 2 mol% or more and less than 93 mol% and an amount of 5 mol% or more and less than 96 mol%, respectively, relative to a sum total of (a), (b) and (c).

[Claim 8]

The method for producing the polyfunctional vinyl aromatic copolymer according to claim 7, wherein the Lewis acid catalyst (f) is a metal fluoride or a complex thereof.

[Claim 9]

The method for producing the polyfunctional vinyl aromatic copolymer according to claim 7, wherein the promoter is at least one compound selected from the group consisting of an ester-based compound, a ketone-based compound, an ether-based compound, and a compound represented by the following formula (2):



(2)

wherein R3 and R4 each independently represent an alkyl group having 1 to 6 carbon atoms, or an aromatic hydrocarbon group having 6 to 30 carbon atoms, and

R5 represents hydrogen, an alkyl group having 1 to 6 carbon atoms, or an aromatic hydrocarbon group having 6 to 30 carbon atoms.