

Description

Title of Invention:

POLYVALENT HYDROXY RESIN, EPOXY RESIN, METHOD FOR PRODUCING SAME,
EPOXY RESIN COMPOSITION AND CURED PRODUCT THEREOF

Technical Field

[0001] The present invention relates to: an epoxy resin that is excellent in curability and provides a cured product excellent in mechanical strength, flame retardancy, moisture resistance, and low elasticity; a polyvalent hydroxy resin suitable for an intermediate thereof; production methods therefor; epoxy resin compositions using the resins; and cured products thereof, which are suitably used for insulating materials in electrical and electronic fields, such as a semiconductor sealant and a printed-wiring board.

Background Art

[0002] Epoxy resins have been industrially used in a wide range of applications, and in recent years, have been required to have further sophisticated performance. For example, a resin composition containing an epoxy resin as a base compound is typically used in the field of a semiconductor sealing material, and development of a material excellent in solder heat resistance has been required because the degree of integration of semiconductor elements is improved to cause an increase in package area and a decrease in

package thickness as well as progress of transition to a surface mounting system as a mounting system. Therefore, the sealing material is strongly desired to have lowered hygroscopicity and improved adhesion property and adhesiveness at an interface between different kinds of materials such as a lead frame and a chip. As in the case of the semiconductor sealing material, there has been desired development of a circuit board material that has improved low hygroscopicity, high heat resistance, and high adhesiveness, from the viewpoint of improving solder heat resistance, and is excellent in low dielectricity from the viewpoint of reducing a dielectric loss. To meet such requirements, various epoxy resins and curing agents having novel structures have been studied. Further, recently, there is a move to eliminate halogen-based flame retardants from the viewpoint of reducing environmental loads, and an epoxy resin and a curing agent more excellent in flame retardancy have been required.

[0003] Therefore, under the above-mentioned circumstances, various epoxy resins and epoxy resin curing agents have been studied. A naphthalene-based resin is known as one example of the epoxy resin curing agents. Patent Literature 1 discloses that a naphthol aralkyl resin is applied to a semiconductor sealant and is excellent in flame retardancy, low hygroscopicity, low thermal expansivity, and the like. Further, Patent Literature 2 proposes a curing agent having a biphenyl structure, and discloses that the agent is effective for improving flame retardancy. However, both of the naphthol

aralkyl resin and the biphenyl aralkyl resin are inferior in curability and may have an insufficient effect of improving flame retardancy.

[0004] On the other hand, epoxy resins that meet such requirements have not yet been known. For example, a known bisphenol-type epoxy resin is widely used because the resin is in a liquid state at normal temperature, is excellent in workability, and can be readily mixed with a curing agent, an additive, or the like. However, the resin is inferior in heat resistance and moisture resistance. In addition, an o-cresol novolac-type epoxy resin is known to have improved heat resistance, but has insufficient flame retardancy.

[0005] As a strategy for improving the flame retardancy without using a halogen-based flame retardant, there is disclosed a method involving adding a phosphate-based flame retardant. However, the method involving using the phosphate-based flame retardant cannot achieve sufficient moisture resistance. In addition, a phosphate may undergo hydrolysis under a high-temperature and high-humidity environment, resulting in reduction of reliability as an insulating material.

[0006] Patent Literatures 2 and 3 disclose examples of applications of aralkyl-type epoxy resins each having a biphenyl structure to a semiconductor sealant as substances containing no phosphorus atom or no halogen atom and capable of improving the flame retardancy. In Patent Literature 4, there is disclosed an

example of use of an aralkyl-type epoxy resin having a naphthalene structure. However, the epoxy resins exhibit unsatisfactory performance in flame retardancy, moisture resistance, or heat resistance.

[0007] Patent Literature 5 discloses a benzylated polyphenol and an epoxy resin thereof as an example developed with focusing attention on improvement of heat resistance, moisture resistance, and crack resistance, but the substances are not ones developed with focusing attention on the flame retardancy. In addition, Patent Literature 6 discloses a production method for a styrene-modified novolac, but the substance is not one developed with focusing attention as an epoxy resin composition.

[0008] Further, Patent Literatures 7 and 8 disclose styrene-modified phenol novolac resins and epoxy resin compositions using the epoxy resins as examples of an epoxy resin composition developed with focusing attention on improvement of moisture resistance and low stress. However, such examples have not been studied in detail on the molecular weight distribution of the styrenated phenol novolac and epoxy resins. It should be noted that the molecular weight distribution (dispersion) is represented as M_w/M_n .

[0009] On the other hand, Patent Literature 9 discloses a styrene-modified phenol novolac resin and an epoxy resin composition using the epoxy resin as an example developed with focusing attention on improvement of flame retardancy. This literature focuses

attention on the amount of modification with styrene, and there is used a resin having a high hydroxy group equivalent or a high epoxy equivalent adjusted by increasing the amount of modification. It is known that, when the content of an aliphatic component derived from an epoxy group is relatively reduced in a cured product using such resin, the cured product can exhibit high flame retardancy. However, in this literature, there is no detail study on the molecular weight distribution of a polyvalent hydroxy resin and an epoxy resin.

Citation List

Patent Literature

[0010]

[PTL 1] JP 2005-344081 A

[PTL 2] JP 11-140166 A

[PTL 3] JP 2000-129092 A

[PTL 4] JP 2004-59792 A

[PTL 5] JP 8-120039 A

[PTL 6] JP 48-52895 A

[PTL 7] JP 5-132544 A

[PTL 8] JP 5-140265 A

[PTL 9] JP 2010-235819 A

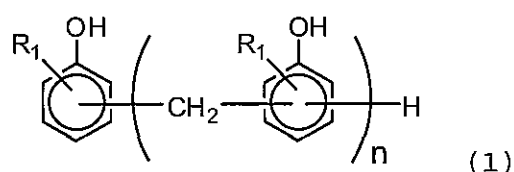
Summary of Invention

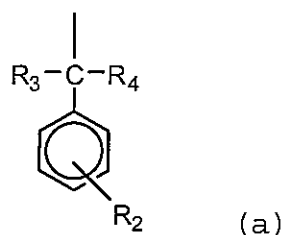
[0011] An object of the present invention is to provide: an epoxy resin that is excellent in curability and mechanical physical

properties and has excellent performance such as flame retardancy, moisture resistance, and low elasticity in applications such as lamination, molding, casting, and adhesion; an epoxy resin composition that has excellent curability and mechanical properties, provides a cured product excellent in flame retardancy, moisture resistance, low elasticity, and the like, and is suitable for sealing of electrical and electronic parts, circuit board materials, and the like; and a cured product thereof.

[0012] That is, the present invention relates to an aralkyl-modified polyvalent hydroxy resin, which is obtained by subjecting a polyvalent hydroxy compound represented by the following general formula (1) to a reaction with an aralkylating agent to substitute a benzene ring in the polyvalent hydroxy compound by an aralkylating agent-derived substituent represented by the formula (a), the aralkyl-modified polyvalent hydroxy resin being obtained by using, as the polyvalent hydroxy compound represented by the general formula (1), a narrowly dispersed polyvalent hydroxy compound including, in terms of area% measured by gel permeation chromatography (GPC), 15% or less of n=1 component and 50% or more of a total of n=2 and n=3 components and having an Mw/Mn of 1.2 or less.

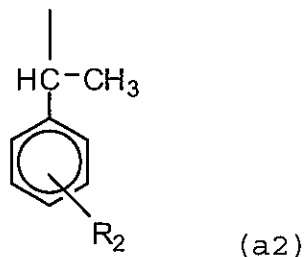
[0013]





(In the formulae, R_1 and R_2 each represent a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, R_3 and R_4 each represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, and n represents a number of from 1 to 5.

[0014] According to another aspect of the present invention, there is provided a styrene-modified polyvalent hydroxy resin obtained by subjecting a polyvalent hydroxy compound represented by the general formula (1) to a reaction with a styrene to substitute a benzene ring in the polyvalent hydroxy compound by a styrene-derived substituent represented by the formula (a2), the styrene-modified polyvalent hydroxy resin being obtained by using, as the polyvalent hydroxy compound represented by the general formula (1), a narrowly dispersed polyvalent hydroxy compound including, in terms of area% measured by GPC, 15% or less of $n=1$ component and 50% or more of a total of $n=2$ and $n=3$ components and having an M_w/M_n of 1.2 or less:

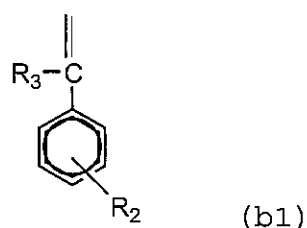


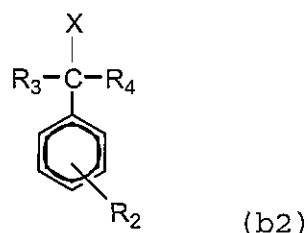
(In the formula, R_2 has the same meaning as that defined for the

formula (a).)

[0015] According to another aspect of the present invention, there is provided a production method for an aralkyl-modified polyvalent hydroxy resin, the production method including producing an aralkyl-modified polyvalent hydroxy resin, which is obtained by subjecting a polyvalent hydroxy compound represented by the general formula (1) to a reaction with an aralkylating agent represented by the following formula (b1) or (b2) to substitute a benzene ring in the polyvalent hydroxy compound by an aralkylating agent-derived substituent represented by the formula (a), using, as the polyvalent hydroxy compound represented by the general formula (1), a narrowly dispersed polyvalent hydroxy compound including, in terms of area% measured by GPC, 15% or less of n=1 component and 50% or more of a total of n=2 and n=3 components and having an Mw/Mn of 1.2 or less, the reaction being performed in the presence of from 10 to 1,000 ppm of an acid catalyst at a reaction temperature of from 40 to 120°C.

[0016]





(In the formulae, R₂ represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, R₃ and R₄ each represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, X represents a halogen, OH, or OR₅, and R₅ represents an alkyl group having 1 to 6 carbon atoms.)

[0017] In the production method for an aralkyl-modified polyvalent hydroxy resin, it is preferred that: the reaction include subjecting from 0.1 to 1.5 mol of the aralkylating agent to a reaction with 1 mol of a hydroxy group in the polyvalent hydroxy compound; or the aralkylating agent include styrene.

[0018] According to another aspect of the present invention, there are provided: an epoxy resin composition, including an epoxy resin and a curing agent, the epoxy resin composition being obtained by using, as a part or whole of the curing agent, the aralkyl-modified polyvalent hydroxy resin as an essential component; and a cured product thereof.

[0019] According to another aspect of the present invention, there is provided an epoxy resin, which is obtained by subjecting the aralkyl-modified polyvalent hydroxy resin to a reaction with epichlorohydrin. In addition, according to another aspect of the present invention, there is provided a production method for an

epoxy resin, the production method including subjecting the aralkyl-modified polyvalent hydroxy resin to a reaction with epichlorohydrin to convert a hydroxy group in the aralkyl-modified polyvalent hydroxy resin into a glycidyl ether group.

[0020] According to another aspect of the present invention, there are provided: an epoxy resin composition, including an epoxy resin and a curing agent, the epoxy resin composition being obtained by blending the epoxy resin as an essential component; and an epoxy resin cured product thereof.

Brief Description of Drawings

[0021] FIG. 1 is a GPC chart of a polyvalent hydroxy compound A.

FIG. 2 is a GPC chart of a polyvalent hydroxy compound B.

FIG. 3 is a GPC chart of a polyvalent hydroxy compound C.

FIG. 4 is a GPC chart of a modified polyvalent hydroxy resin A.

FIG. 5 is a GPC chart of a modified polyvalent hydroxy resin B.

FIG. 6 is a GPC chart of a modified polyvalent hydroxy resin C.

FIG. 7 is a GPC chart of a modified polyvalent hydroxy resin D.

FIG. 8 is a GPC chart of an epoxy resin A.

FIG. 9 is a GPC chart of an epoxy resin B.

FIG. 10 is a GPC chart of an epoxy resin C.

FIG. 11 is a GPC chart of an epoxy resin D.

Description of Embodiments

[0022] In an epoxy resin cured product, a hydroxypropyl group

generated through a reaction of an epoxy group with a hydroxy group is known to be highly combustible. However, when an aralkyl group is added to a polyvalent hydroxy compound to increase a hydroxy group equivalent, the aliphatic carbon ratio of combustible components derived from the epoxy group becomes lower, which enables expression of high flame retardancy. Further, addition of the aralkyl group with high aromaticity additionally improves aromaticity of the polyvalent hydroxy resin and is effective for improving moisture resistance in addition to the flame retardancy.

[0023] On the other hand, however, the technique for improving physical properties by increasing the ratio of modification with the aralkyl group was found to tend to cause deterioration of curability owing to an increase in steric hindrance and deterioration of mechanical strength of a cured product. Therefore, when the molecular weight distribution of a polyvalent hydroxy compound used as a base was controlled, there were obtained aralkyl-modified polyvalent hydroxy resin and epoxy resin, which are excellent in curability and mechanical strength and are also excellent in flame retardancy, moisture resistance, and low elasticity, at a ratio of modification with the aralkyl group, which does not impair curability and mechanical strength.

[0024] The polyvalent hydroxy compound to be used in the present invention is a narrowly dispersed polyvalent hydroxy compound represented by the general formula (1), and hence is also referred to as polyvalent hydroxy compound (1) or narrowly dispersed

polyvalent hydroxy compound. In addition, the compound is one kind of novolac resin, and hence is also referred to as phenol novolac.

[0025] When an aralkyl-modified polyvalent hydroxy resin and epoxy resin including the narrowly dispersed polyvalent hydroxy compound as a base are used, epoxy resin compositions excellent in curability, mechanical strength, flame retardancy, and the like can be obtained. That is, in the case where the ratio of aralkyl-modified products of the $n=1$ (bifunctional) component of the polyvalent hydroxy compound increases, steric hindrance tends to increase to deteriorate curability and to lower mechanical strength of a cured product. On the other hand, in the cases of using a polyvalent hydroxy compound having a high ratio of $n=2$ (trifunctional) and $n=3$ (tetrafunctional) components as more polyfunctional components, the effect of steric hindrance is relatively reduced even when the components are modified with aralkyl groups. Therefore, a cured product excellent in curability and mechanical strength can be obtained. In addition, in the case where polyfunctional components increase, the crosslinking density of the cured product tends to increase to produce a cured product having more excellent heat stability and excellent flame retardancy. However, in the case where $n=4$ (pentafunctional) or more components increase, the molecular weights increase, resulting in deterioration of fluidity and molding processability.

[0026] Therefore, when the resins are used, it is possible to produce epoxy resin compositions excellent in curability, mechanical

strength, flame retardancy, and the like, in particular, epoxy resin compositions for sealing a semiconductor. That is, the compositions exhibit excellent curability and physical properties excellent in mechanical strength, high flame retardancy, moisture resistance, and low elasticity, and the raw materials are used to produce, for example, reliable materials for sealing of electrical and electronic parts or for circuit boards.

[0027] Firstly, the aralkyl-modified polyvalent hydroxy resin (StPN) of the present invention is described. The aralkyl-modified polyvalent hydroxy resin of the present invention can be obtained by subjecting a narrowly dispersed polyvalent hydroxy compound used as a polyvalent hydroxy compound represented by the general formula (1), which includes, in terms of area% detected by gel permeation chromatography (GPC; RI), 15% or less of $n=1$ component and 50% or more of a total of $n=2$ and $n=3$ components, and has an M_w/M_n of 1.2 or less, to a reaction with an aralkylating agent.

[0028] The aralkyl-modified polyvalent hydroxy resin of the present invention is referred to as StPN, and the polyvalent hydroxy compound that is used for producing the resin and is represented by the general formula (1) is referred to as polyvalent hydroxy compound or narrowly dispersed polyvalent hydroxy compound. The aralkyl in the aralkyl-modified polyvalent hydroxy resin refers to a group represented by the formula (a). The aralkylating agent to be used for producing the StPN refers to a compound represented by the formula (c1) or (c2). In addition, the aralkylating agent

may be typified by styrene, and the aralkyl-modified polyvalent hydroxy resin may also be referred to as styrene-modified polyvalent hydroxy resin.

[0029] The range of the molecular weight distribution of the narrowly dispersed polyvalent hydroxy compound to be used in the present invention is as described below. The range of the content of the $n=1$ component is 15% or less, more preferably 10% or less. In addition, the range of the content of the $n=2$ and $n=3$ components is 50% or more, more preferably 60% or more, even more preferably 70% or more. When the content of the $n=1$ component is reduced, it is possible to improve physical properties such as curability, mechanical strength, and flame retardancy. Further, the range of the molecular weight distribution (M_w/M_n) is preferably 1.2 or less, more preferably 1.1 or less. When the molecular weight distribution exceeds 1.2, physical properties such as curability and mechanical strength tend to deteriorate. It should be noted that the GPC area% is approximately proportional to wt%, and hence the GPC area% can be considered as wt%.

[0030] The narrowly dispersed polyvalent hydroxy compound to be used in the present invention can be obtained by removing low-molecular-weight components from a crude polyvalent hydroxy compound obtained by adjusting the molar ratio of an aldehyde to a phenol.

[0031] The molar ratio of the aldehyde to the phenol is represented as a molar ratio of the aldehyde to 1 mol of the phenol,

and the narrowly dispersed polyvalent hydroxy compound is produced in the range of from 0.1 to 0.9. When the molar ratio is small, n=1 to 3 components are produced in large amounts, while when the molar ratio is large, n=1 to 3 components are produced in small amounts because n=4 or more components having high molecular weights are produced in large amounts.

[0032] The narrowly dispersed polyvalent hydroxy compound to be used in the present invention can be obtained by, for example, a method of producing the compound by a step of subjecting a phenol to a reaction with an aldehyde in the presence of a phosphate catalyst in a heterogeneous system, a method involving removing n=1 component and/or n=4 or more components having high molecular weights from a crude polyvalent hydroxy compound to be obtained based on a difference in solubility in various solvents, or a method involving dissolving a dinuclear compound in an aqueous alkaline solution and removing unnecessary components. The narrowly dispersed polyvalent hydroxy compound may be obtained by another known separation method.

[0033] The StPN of the present invention is obtained by subjecting the narrowly dispersed polyvalent hydroxy compound represented by the general formula (1) to an addition reaction with the aralkylating agent. In this case, the ratio of the aralkylating agent to the polyvalent hydroxy compound is as described below. In consideration of a balance between flame retardancy and curability of a cured product to be obtained, the ratio of the aralkylating

agent used to 1 mol of the polyvalent hydroxy compound falls within the range of preferably from 0.1 to 1.5 mol, more preferably from 0.1 to 1.0 mol, even more preferably from 0.3 to 0.8 mol. When the ratio is smaller than the values, the properties of the polyvalent hydroxy compound used as a raw material remain unimproved, while when the ratio is larger than the values, curability tends to deteriorate because the density of functional groups becomes too low.

[0034] In this reaction, the aralkylating agent is added to an aromatic ring having an OH group in the polyvalent hydroxy compound to substitute the aromatic ring by the aralkyl group represented by the formula (a). In the formula (a), R_3 and R_4 each represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms. It is preferred that the alkyl group be a methyl group. It is more preferred that one or both of R_3 and R_4 represent a hydrogen atom or a methyl group, and it is even more preferred that one or both of R_3 and R_4 each represent a hydrogen atom. When both of R_3 and R_4 each represent a hydrogen atom, the group is a benzyl group. When one of R_3 and R_4 represents a hydrogen atom, the group is an α -alkyl-substituted benzyl group. A benzene ring in the benzyl group or the α -alkyl-substituted benzyl group may be substituted by a substituent R_2 . The position to which the aralkyl group is added may be a free ortho and/or para position in the polyvalent hydroxy compound, and is typically a para position.

[0035] In addition, the StPN of the present invention preferably

has a melt viscosity at 150°C within the range of from 0.01 to 10.0 Pa·s. From the viewpoint of workability, the melt viscosity is preferably as low as possible within the range.

[0036] Further, the StPN of the present invention suitably has a softening point within the range of from 40 to 150°C, preferably from 50 to 100°C. Herein, the softening point refers to a softening point measured based on the ring-and-ball method of JIS-K-2207. When the softening point is lower than the value, a cured product obtained from an epoxy resin including the StPN blended therein has lowered heat resistance. When the softening point is higher than the value, fluidity in molding deteriorates.

[0037] The amount of the aralkyl group to be added can be adjusted based on the amount of the aralkylating agent used, and generally, 0.1 to 2.5 aralkyl groups are added to the benzene ring in the polyvalent hydroxy compound. This number means an average number (number average) of the aralkyl groups to be substituted for one phenol ring. The amount of the aralkyl group to be added is preferably from 0.1 to 1.5 mol, more preferably from 0.1 to 1.0 mol, even more preferably from 0.3 to 0.8 mol, with respect to 1 mol of the benzene ring in the polyvalent hydroxy compound. It should be noted that maximum four aralkyl groups may be substituted for the phenol rings at both ends, and up to three aralkyl groups may be substituted for the phenol ring located at the midpoint. Therefore, when n represents 1, up to eight aralkyl groups may be substituted.

[0038] In the formula (a), R₂ represents hydrogen or a

hydrocarbon group having 1 to 6 carbon atoms, preferably hydrogen or an alkyl group having 1 to 3 carbon atoms, more preferably hydrogen. The R_2 is determined based on the aralkylating agent to be used as a reaction raw material.

[0039] In the general formula (1), n represents a number of from 1 to 5. It is preferred that n represent a number within the range of from 1.9 to 3.4 as an average (number average). It is more preferred that n represent a number within the range of from 2.0 to 3.0, but it is necessary to satisfy the dispersion. From another viewpoint, the compound suitably includes components in which n represents from 1 to 5 as major components. The major components refer to components that are contained at 80 wt% or more, preferably 90 wt% or more, more preferably substantially 100%. In the general formula (1), R_1 represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, preferably a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

[0040] Next, a production method for the StPN of the present invention is described. A phenol novolac is suited for the polyvalent hydroxy compound that is used in the production method for the StPN of the present invention and is represented by the general formula (1). The phenol novolac is obtained from a phenol and an aldehyde.

[0041] Phenol is mainly used as the phenol used for obtaining the polyvalent hydroxy compound. The phenol may contain a small amount of any other phenol component. Examples thereof include o-cresol, m-cresol, p-cresol, an ethylphenol, an isopropylphenol,

a tert-butylphenol, an allylphenol, and a phenylphenol. One kind of those phenols may be used alone, or two or more kinds thereof may be used in combination. It should be noted that there may be blended any other phenol or a naphthol such as 2,6-xylenol, 2,6-diethylphenol, hydroquinone, resorcin, catechol, 1-naphthol, 2-naphthol, 1,5-naphthalenediol, 1,6-naphthalenediol, 1,7-naphthalenediol, 2,6-naphthalenediol, or 2,7-naphthalenediol when the amount thereof is small. When any one of those is blended, the amount thereof is desirably limited to 30 wt% or less, preferably 20 wt% or less.

[0042] As the aralkylating agent to be used in the reaction with the polyvalent hydroxy compound, there is used a compound represented by the formula (c1) or (c2). A compound represented by the formula (c1) is referred to as styrene. The styrene includes styrene or styrene substituted by a hydrocarbon group having 1 to 6 carbon atoms. In the formula (c1), R₃ represents hydrogen or an alkyl group having 1 to 6 carbon atoms, preferably hydrogen. The styrene may contain a small amount of another reactive component, and examples of the other reactive component include unsaturated bond-containing components such as divinylbenzene, indene, coumarone, benzothiophene, indole, and vinyl naphthalene. When any one of the components is blended, the amount thereof is desirably limited to 30 wt% or less, preferably 20 wt% or less.

[0043] In the formula (c2), R₂, R₃, and R₄ have the same meanings as R₂, R₃, and R₄ defined for the formula (a). X represents a halogen

atom, an alkoxy group having 1 to 6 carbon atoms, or a hydroxy group. In the formula (c1), R₂ and R₃ have the same meanings as R₂ and R₃ defined for the formula (a).

[0044] When X represents a halogen atom, examples of the aralkylating agent represented by the formula (c2) include benzyl chloride, benzyl bromide, benzyl iodide, o-methylbenzyl chloride, m-methylbenzyl chloride, p-methylbenzyl chloride, p-ethylbenzyl chloride, p-isopropylbenzyl chloride, p-tert-butylbenzyl chloride, p-cyclohexylbenzyl chloride, p-phenylbenzyl chloride, α -methylbenzyl chloride, and α,α -dimethylbenzyl chloride. When X represents an alkoxy group, an alkoxy group having 1 to 4 carbon atoms is preferred, and examples of the aralkylating agent include benzyl methyl ether, o-methylbenzyl methyl ether, m-methylbenzyl methyl ether, p-methylbenzyl methyl ether, p-ethylbenzyl methyl ether, benzyl ethyl ether, benzyl isopropyl ether, benzyl n-propyl ether, benzyl isobutyl ether, benzyl n-butyl ether, and p-methylbenzyl methyl ether. When X represents a hydroxy group, examples of the aralkylating agent include benzyl alcohol, o-methylbenzyl alcohol, m-methylbenzyl alcohol, p-methylbenzyl alcohol, p-ethylbenzyl alcohol, p-isopropylbenzyl alcohol, p-tert-butylbenzyl alcohol, p-cyclohexylbenzyl alcohol, p-phenylbenzyl alcohol, α -methylbenzyl alcohol, and α,α -dimethylbenzyl alcohol. Examples of the aralkylating agent represented by the formula (c1) include styrene, an alkyl styrene obtained by subjecting a benzene ring of styrene to substitution

by an C1 to 6 alkyl group, and an α -alkylstyrene. Of those, an alkylstyrene or styrene is preferred, and styrene is more preferred.

[0045] The aralkylation reaction using the aralkylating agent can be performed in the presence of an acid catalyst, and the amount of the catalyst used falls within the range of from 10 to 1,000 ppm (wt), preferably from 100 to 500 ppm. When the amount is larger than the values, a methylene cross-linking bond in the polyvalent hydroxy compound is readily cleaved. A monovalent phenol component obtained as a by-product in the cleavage reaction deteriorates curability and heat resistance. On the other hand, when the amount is smaller than the values, reactivity lowers, resulting in an increase in the amount of unreacted aralkylating agent. In addition, the term "amount of the catalyst" as used herein refers to an amount of the catalyst with respect to the total weight of the polyvalent hydroxy compound and aralkylating agent to be used in the reaction.

[0046] The acid catalyst may appropriately be selected from well-known inorganic acids and well-known organic acids. Examples thereof include: a mineral acid such as hydrochloric acid, sulfuric acid, or phosphoric acid; an organic acid such as folic acid, oxalic acid, trifluoroacetic acid, p-toluenesulfonic acid, dimethyl sulfate, or diethyl sulfate; a Lewis acid such as zinc chloride, aluminum chloride, iron chloride, or boron trifluoride; and a solid acid such as an ion exchange resin, activated clay, silica-alumina, or zeolite.

[0047] In addition, the reaction is performed at a reaction

temperature within the range of from 40 to 120°C. When the temperature is lower than the values, reactivity lowers, resulting in extension of the reaction time. In addition, when the temperature is higher than the values, part of the methylene cross-linking bond in the polyvalent hydroxy compound is readily cleaved. A monovalent phenol component obtained as a by-product in the cleavage reaction deteriorates curability and heat resistance.

[0048] In addition, the reaction is generally performed for from 1 to 20 hours. Further, in the reaction, as a solvent, there may be used, for example: an alcohol such as methanol, ethanol, propanol, butanol, ethylene glycol, methyl cellosolve, or ethyl cellosolve; a ketone such as acetone, methyl ethyl ketone, or methyl isobutyl ketone; an ether such as dimethyl ether, diethyl ether, diisopropyl ether, tetrahydrofuran, or dioxane; and an aromatic compound such as benzene, toluene, chlorobenzene, or dichlorobenzene.

[0049] Specifically, in general, the reaction is performed by a method involving feeding all raw materials at once and allowing the mixture to react at a predetermined temperature or by a method involving feeding a polyvalent hydroxy compound and a catalyst and allowing the mixture to react while an aralkylating agent is added dropwise at a predetermined temperature. In this case, the time for dropwise addition is preferably 5 hours or less, generally from 1 to 10 hours. In the case of using a solvent, if necessary, the catalyst component is removed after the reaction, and the solvent

may be distilled off to afford the resin of the present invention. In the case of using no solvent, hot discharge may be directly performed to afford a product of interest.

[0050] Next, the epoxy resin (StPNE) of the present invention is described.

The epoxy resin (StPNE) of the present invention can be obtained by epoxidizing the StPN.

[0051] The StPNE of the present invention is advantageously produced by subjecting the StPN to a reaction with epichlorohydrin. The reaction of the StPN with epichlorohydrin can be performed in the same manner as a general epoxidation reaction.

[0052] An example of the method is a method involving: dissolving the StPN in an excessive amount of epichlorohydrin; and allowing the mixture to react in the presence of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide at from 20 to 150°C, preferably at from 30 to 80°C for from 1 to 10 hours. In this case, the amount of the alkali metal hydroxide used falls within the range of from 0.8 to 1.5 mol, preferably from 0.9 to 1.2 mol, with respect to 1 mol of a hydroxy group in the StPN. In addition, epichlorohydrin is used in an excessive amount with respect to 1 mol of a hydroxy group in the StPN, and the amount generally falls within the range of from 1.5 to 30 mol, preferably from 2 to 15 mol, with respect to 1 mol of a hydroxy group in the StPN. After completion of the reaction, the excessive amount of epichlorohydrin is distilled off, and the residue is dissolved in

a solvent such as toluene or methyl isobutyl ketone. The resultant is filtered and washed with water to remove inorganic salts, and the solvent is distilled off to afford an epoxy resin of interest.

[0053] The epoxy resin composition of the present invention includes at least an epoxy resin and a curing agent, and examples thereof include the following three kinds of compositions.

- 1) A composition including the StPNE blended as a part or whole of the epoxy resin.
- 2) A composition including the StPN blended as a part or whole of the curing agent.
- 3) A composition including the StPNE and StPN blended as a part or whole of the epoxy resin and curing agent.

[0054] The compositions according to the above-mentioned items 2) and 3) include the StPN as an essential component. The amount of the StPN to be blended generally falls within the range of from 2 to 200 parts by weight, preferably from 5 to 80 parts by weight, with respect to 100 parts by weight of the epoxy resin. When the amount is smaller than the values, there is a problem in that improving effects on flame retardancy and moisture resistance are small, while when the amount is larger than the values, there is a problem in that moldability and strength of the cured product deteriorate.

[0055] In the case where the StPN is used as a total amount of the curing agent, the amount of the StPN to be blended is generally determined in consideration of an equivalent balance between the OH group in the StPN and the epoxy group in the epoxy resin. The

equivalent ratio between the epoxy resin and the curing agent generally falls within the range of from 0.2 to 5.0, preferably from 0.5 to 2.0. When the equivalent ratio is larger or smaller than the values, curability of the epoxy resin composition deteriorates, and heat resistance, mechanical strength, and the like of the cured product deteriorate.

[0056] As the curing agent, a curing agent other than the StPN may be used in combination with the StPN. The amount of the other curing agent to be blended is determined so that the amount of the StPN to be blended generally falls within the range of from 2 to 200 parts by weight, preferably from 5 to 80 parts by weight, with respect to 100 parts by weight of the epoxy resin. When the StPN to be blended is smaller than the values, there is a problem in that improving effects on low hygroscopicity, adhesiveness, and flame retardancy are small. When the StPN to be blended is larger than the values, there is a problem in that moldability and strength of the cured product deteriorate. In this case, the equivalent ratio between the epoxy resin and the curing agent (total) is adjusted within the range described above.

[0057] All compounds that are generally known as curing agents for epoxy resins may be used as the curing agent other than the StPN, and examples thereof include dicyandiamide, an acid anhydride, a polyhydric phenol, and aromatic and aliphatic amines. Of those, a polyhydric phenol is preferably used as the curing agent in the field requiring high electrical insulation property, such as a

semiconductor sealant. In the case of a composition including the StPN of the present invention as an essential component, the amount of the StPN to be blended desirably falls within the range of from 50 to 100%, preferably 60 to 100%, with respect to the whole of the curing agent. Specific examples of the curing agent other than the StPN are described below.

[0058] Examples of the acid anhydride curing agent include phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methylhimic anhydride, dodecynylsuccinic anhydride, nadic anhydride, and trimellitic anhydride.

[0059] Examples of the polyhydric phenol include: a dihydric phenol such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, or naphthalenediol; and a tri- or higher hydric phenol typified by, for example, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, o-cresol novolac, naphthol novolac, or polyvinyl phenol. A further example thereof is a polyhydric phenolic compound synthesized from a phenol, a naphthol, or a dihydric phenol such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, or naphthalenediol, and a condensing agent such as formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, p-xylylene dichloride,

bis(chloromethyl)biphenyl, or bis(chloromethyl)naphthalene.

[0060] Examples of the amine include: an aromatic amine such as 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenyl sulfone, m-phenylenediamine, or p-xylylenediamine; and an aliphatic amine such as ethylenediamine, hexamethylenediamine, diethylenetriamine, or triethylenetetramine.

In the composition, one kind of those curing agents may be used alone, or two or more kinds thereof may be used as a mixture.

[0061] The epoxy resin to be used in the composition is selected from epoxy resins each having two or more epoxy groups per molecule. Examples thereof include: an epoxidized product of a dihydric phenol such as bisphenol A, bisphenol F, 3,3',5,5'-tetramethyl-bisphenol F, bisphenol S, fluorene bisphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenol, resorcin, or naphthalenediol; an epoxidized product of a tri- or more hydric phenol such as tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, or o-cresol novolac; an epoxidized product of a co-condensation resin of dichloropentadiene and a phenol; an epoxidized product of a phenol aralkyl resin synthesized from a phenol, paraxylylene dichloride, and the like; an epoxidized product of a biphenyl aralkyl-type phenol resin synthesized from a phenol, bischloromethyl biphenyl, and the like; and an epoxidized product of a naphthol aralkyl resin synthesized from a naphthol, paraxylylene dichloride, and the like.

One kind of those epoxy resins may be used alone, or two or more kinds thereof may be used as a mixture.

[0062] The compositions according to the above-mentioned items 1) and 3) each include the StPNE as an essential component. Another kind of epoxy resin other than the StPNE may be blended as an epoxy resin component in the epoxy resin composition. As the epoxy resin in this case, there may be used all general epoxy resins each having two or more epoxy groups in the molecule. Examples thereof include glycidyl-etherified products derived from: a dihydric phenol such as bisphenol A, bisphenol S, fluorene bisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, or resorcin; a tri- or more hydric phenol such as tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, or o-cresol novolac; a phenol-based aralkyl resin; a biphenyl aralkyl resin; a naphthol-based aralkyl resin; or a halogenated bisphenol such as tetrabromobisphenol A. One kind of those epoxy resins may be used alone, or two or more kinds thereof may be used as a mixture. In the case of a composition including the StPNE of the present invention as an essential component, the amount of the StPNE to be blended desirably falls within the range of from 50 to 100%, preferably from 60 to 100%, with respect to the whole of the epoxy resin.

[0063] In the epoxy resin composition of the present invention, there may be appropriately blended, as another modifier or the like, an oligomer or polymer compound such as polyester, polyamide,

polyimide, polyether, polyurethane, a petroleum resin, an indene resin, an indene/coumarone resin, or a phenoxy resin. The amount of the modifier to be added generally falls within the range of from 2 to 30 parts by weight with respect to 100 parts by weight of the epoxy resin.

[0064] In addition, an additive such as an inorganic filler, a pigment, a flame retardant, a thixotropy-imparting agent, a coupling agent, or a fluidity improver may be blended in the epoxy resin composition of the present invention. Examples of the inorganic filler include spherical or crushed molten silica, silica powder such as crystalline silica, alumina powder, glass powder, mica, talc, calcium carbonate, alumina, and hydrated alumina. When the composition is used for a semiconductor sealant, the amount of the additive to be blended is preferably 70 wt% or more, more preferably 80 wt% or more.

[0065] The pigment includes an organic or inorganic extender pigment, a scaly pigment, and the like. Examples of the thixotropy-imparting agent include a silicon-based thixotropy-imparting agent, a castor oil-based thixotropy-imparting agent, an aliphatic amide wax, an oxidized polyethylene wax, and an organic bentonite-based thixotropy-imparting agent.

[0066] Further, if necessary, a curing accelerator may be used in the epoxy resin composition of the present invention. Examples thereof include an amine, an imidazole, an organic phosphine, and

a Lewis acid. Specific examples thereof include: a tertiary amine such as 1,8-diazabicyclo(5,4,0)undecene-7, triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, or tris(dimethylaminomethyl)phenol; an imidazole such as 2-methylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 2-phenyl-4-methylimidazole, or 2-heptadecylimidazole; an organic phosphine such as tributylphosphine, methyldiphenylphosphine, triphenylphosphine, diphenylphosphine, or phenylphosphine; a tetra-substituted phosphonium tetra-substituted borate such as tetraphenylphosphonium tetraphenylborate, tetraphenylphosphonium ethyltriphenylborate, or tetrabutylphosphonium tetrabutylborate; and a tetraphenylborate such as 2-ethyl-4-methylimidazole tetraphenylborate or N-methylmorpholine tetraphenylborate. The amount of the accelerator to be added generally falls within the range of from 0.2 to 5 parts by weight with respect to 100 parts by weight of the epoxy resin.

[0067] If necessary, in the resin composition of the present invention, there may be further used: a mold release agent such as carnauba wax or OP wax; a coupling agent such as γ -glycidoxypropyltrimethoxysilane; a colorant such as carbon black; a flame retardant such as antimony trioxide; a stress-lowering agent such as silicon oil; or a lubricant such as calcium stearate.

[0068] The epoxy resin composition of the present invention may be used to prepare a prepreg by dissolving the composition in an organic solvent to prepare a varnish, impregnating a fibrous

product such as a glass cloth, an aramid non-woven fabric, or a polyester non-woven fabric including a liquid crystal polymer with the varnish, and removing the solvent. In addition, in some cases, the composition may be applied onto a sheet-like product such as a copper foil, a stainless foil, a polyimide film, or a polyester film to prepare a laminate.

[0069] When the epoxy resin composition of the present invention is cured by heating, an epoxy resin cured product can be obtained. The cured product is excellent in curability, flame retardancy, low hygroscopicity, low elasticity, and the like. The cured product can be obtained by molding processing of the epoxy resin composition through a method such as cast molding, compression molding, or transfer molding. In this case, the temperature generally falls within the range of from 120 to 220°C.

Examples

[0070] Hereinafter, the present invention is more specifically described by way of Examples. The hydroxy group equivalent and epoxy equivalent are represented in the unit of g/eq.

[0071] Synthesis Example 1

250 g of phenol and 0.75 g of oxalic acid dihydrate as an acid catalyst were loaded into a 1-L four-necked flask, and the mixture was stirred while nitrogen gas was introduced, and was heated to increase the temperature. A dropwise addition of 47.4 g of 37.4% formalin was started at 80°C, and the dropwise addition was completed

in 30 minutes. Further, the mixture was subjected to a reaction for 3 hours while the reaction temperature was kept at 92°C. The mixture was heated up to 110°C while water generated by the reaction was removed to the outside of the system. The residual phenol was recovered at 160°C under reduced pressure. The mixture was further heated to recover part of dinuclear compounds. The resultant polyvalent hydroxy compound was found to have a hydroxy group equivalent of 104, a softening point of 68°C, and a melt viscosity at 150°C of 0.07 Pa·s. The compound was found to have a content of n=1 component of 8.1% and a total content of n=2 and n=3 components of 71.7%, which were measured by GPC, and an Mw/Mn of 1.10. The resin is referred to as polyvalent hydroxy compound A. FIG. 1 shows a GPC chart of the polyvalent hydroxy compound A.

[0072] Synthesis Example 2

250 g of phenol, 47.4 g of 7.4% formalin, and 150 g of 89% phosphoric acid as an acid catalyst were loaded into a 1-L four-necked flask, and the mixture was heated to increase the temperature in a cloudy state (two-phase mixture) formed by mixing with stirring. Further, the mixture was subjected to a reaction for 6 hours while the temperature was kept at a reflux temperature. Subsequently, methyl butyl ketone was added thereto to dissolve a resin component, and the resultant was left to stand still to separate the mixture into a resin solution phase and an aqueous phosphoric acid solution phase. The phosphoric acid solution phase was removed, and the resultant was further washed with water. Subsequently, the residual

phenol was recovered at 160°C under reduced pressure. The mixture was further heated to recover part of dinuclear compounds. The resultant polyvalent hydroxy compound was found to have a hydroxy group equivalent of 103, a softening point of 65°C, and a melt viscosity at 150°C of 0.06 Pa·s. The compound was found to have a content of n=1 component of 2.0% and a total content of n=2 and n=3 components of 91.5%, which were measured by GPC, and an Mw/Mn of 1.04. The resin is referred to as polyvalent hydroxy compound B. FIG. 2 shows a GPC chart of the polyvalent hydroxy compound B.

[0073] Example 1

104 g of the polyvalent hydroxy compound A obtained in Synthesis Example 1 as a polyvalent hydroxy compound component and 0.053 g (300 ppm) of p-toluenesulfonic acid as an acid catalyst were loaded into a 1-L four-necked flask, and the mixture was heated to 120°C. Next, 72.8 g (0.7 mol) of styrene were added dropwise thereto with stirring at 120°C over 3 hours to subject the mixture to a reaction. The mixture was further subjected to a reaction at 120°C for 1 hour to afford 168 g of a styrene-modified polyvalent hydroxy resin. The resin was found to have a hydroxy group equivalent of 177, a softening point of 78°C, and a melt viscosity at 150°C of 0.13 Pa·s. The resin is referred to as modified polyvalent hydroxy resin A (StPN-A). FIG. 4 shows a GPC chart of the StPN-A.

[0074] Example 2

103 g of the polyvalent hydroxy compound B obtained in Synthesis Example 2 as a polyvalent hydroxy compound component and 0.053 g

(300 ppm) of p-toluenesulfonic acid as an acid catalyst were loaded into a 1-L four-necked flask, and the mixture was heated to 120°C. Next, 72.8 g (0.7 mol) of styrene were added dropwise thereto with stirring at 120°C over 3 hours to subject the mixture to a reaction. The mixture was further subjected to a reaction at 120°C for 1 hour to afford 167 g of an aralkyl styrene-modified polyvalent hydroxy resin. The resin was found to have a hydroxy group equivalent of 176, a softening point of 78°C, and a melt viscosity at 150°C of 0.13 Pa·s. The resin is referred to as modified polyvalent hydroxy resin B (StPN-B). FIG. 5 shows a GPC chart of the StPN-B.

[0075] Example 3

104 g of the polyvalent hydroxy compound A obtained in Synthesis Example 1 as a polyvalent hydroxy compound component and 1.0 g of water were loaded into a 1-L four-necked flask, and the mixture was heated to 120°C. Next, 88.6 g (0.7 mol) of benzyl chloride were added dropwise thereto with stirring at 120°C over 3 hours to subject the mixture to a reaction. The mixture was further subjected to a reaction at 120°C for 1 hour to afford 160 g of a benzyl-modified polyvalent hydroxy resin. The resin was found to have a hydroxy group equivalent of 168, a softening point of 70°C, and a melt viscosity at 150°C of 0.09 Pa·s. The resin is referred to as modified polyvalent hydroxy resin C (StPN-C). FIG. 6 shows a GPC chart of the StPN-C.

[0076] Comparative Example 1

105 g of phenol novolac (manufactured by Showa Denko K.K.;

BRG-555 (sometimes referred to as polyvalent hydroxy compound C; FIG. 3 is a GPC chart thereof), the content of $n=1$ component measured by GPC; 25.4%, the total content of the $n=2$ and $n=3$ components; 32.1%, $M_w/M_n=1.45$, hydroxy group equivalent: 105, softening point: 67°C , melt viscosity at 150°C : $0.08\text{ Pa}\cdot\text{s}$) as a polyvalent hydroxy compound component and 0.055 g (300 ppm) of p-toluenesulfonic acid as an acid catalyst were loaded into a 1-L four-necked flask, and the mixture was heated to 120°C . Next, 73 g (0.7 mol) of styrene were added dropwise thereto with stirring at 120°C over 3 hours to subject the mixture to a reaction. The mixture was further subjected to a reaction at 120°C for 1 hour to afford 170 g of a styrene-modified polyvalent hydroxy resin. The resin was found to have a hydroxy group equivalent of 178, a softening point of 78°C , and a melt viscosity at 150°C of $0.13\text{ Pa}\cdot\text{s}$. The resin is referred to as modified polyvalent hydroxy resin D (StPN-D). FIG. 7 shows a GPC chart of the StPN-D.

[0077] Example 4

150 g of the StPN-A obtained in Example 1, 470 g of epichlorohydrin, and 71 g of diethyleneglycol dimethyl ether were loaded into a four-necked separable flask, and were dissolved by stirring. The components were dissolved homogeneously, and 70.6 g of an aqueous solution of 48% sodium hydroxide were added dropwise over 4 hours under reduced pressure of 130 mmHg while the temperature was kept at 65°C . Water and epichlorohydrin obtained by reflux distillation during the dropwise addition were separated by a

separation bath. The reaction was performed while returning epichlorohydrin to a reaction container and removing water to the outside of the system. After completion of the reaction, the resultant salts were removed by filtration, and the resultant was washed with water. Then, epichlorohydrin was distilled off to afford 168 g of an epoxy resin A (StPNE-A). The resultant resin was found to have an epoxy equivalent of 241, a softening point of 56°C, and a melt viscosity at 150°C of 0.12 Pa·s. FIG. 8 shows a GPC chart of the StPNE-A.

[0078] Example 5

150 g of the StPN-B obtained in Example 2, 473 g of epichlorohydrin, and 71 g of diethyleneglycol dimethyl ether were loaded into a four-necked separable flask, and were dissolved by stirring. The components were dissolved homogeneously, and 71.0 g of an aqueous solution of 48% sodium hydroxide were added dropwise over 4 hours under reduced pressure of 130 mmHg while the temperature was kept at 65°C. Water and epichlorohydrin obtained by reflux distillation during the dropwise addition were separated by a separation bath. The reaction was performed while returning epichlorohydrin to a reaction container and removing water to the outside of the system. After completion of the reaction, the resultant salts were removed by filtration, and the resultant was washed with water. Then, epichlorohydrin was distilled off to afford 165 g of an epoxy resin B (StPNE-B). The resultant resin was found to have an epoxy equivalent of 245, a softening point of 55°C, and

a melt viscosity at 150°C of 0.11 Pa·s. FIG. 9 shows a GPC chart of the StPNE-B.

[0079] Example 6

150 g of the StPN-C obtained in Example 3, 495 g of epichlorohydrin, and 74 g of diethyleneglycol dimethyl ether were loaded into a four-necked separable flask, and were dissolved by stirring. The components were dissolved homogeneously, and 74.4 g of an aqueous solution of 48% sodium hydroxide were added dropwise over 4 hours under reduced pressure of 130 mmHg while the temperature was kept at 65°C. Water and epichlorohydrin obtained by reflux distillation during the dropwise addition were separated by a separation bath. The reaction was performed while returning epichlorohydrin to a reaction container and removing water to the outside of the system. After completion of the reaction, the resultant salts were removed by filtration, and the resultant was washed with water. Then, epichlorohydrin was distilled off to afford 185 g of an epoxy resin C (StPNE-C). The resultant resin was found to have an epoxy equivalent of 236, a softening point of 52°C, and a melt viscosity at 150°C of 0.08 Pa·s. FIG. 10 shows a GPC chart of the StPNE-C.

[0080] Comparative Example 2

150 g of the StPN-D obtained in Comparative Example 1, 468 g of epichlorohydrin, and 70 g of diethyleneglycol dimethyl ether were loaded into a four-necked separable flask, and were dissolved by stirring. The components were dissolved homogeneously, and 70.3

g of an aqueous solution of 48% sodium hydroxide were added dropwise over 4 hours under reduced pressure of 130 mmHg while the temperature was kept at 65°C. Water and epichlorohydrin obtained by reflux distillation during the dropwise addition were separated by a separation bath. The reaction was performed while returning epichlorohydrin to a reaction container and removing water to the outside of the system. After completion of the reaction, the resultant salts were removed by filtration, and the resultant was washed with water. Then, epichlorohydrin was distilled off to afford 185 g of an epoxy resin (StPNE-D). The resultant resin was found to have an epoxy equivalent of 246, a softening point of 56°C, and a melt viscosity at 150°C of 0.10 Pa·s. FIG. 11 shows a GPC chart of the StPNE-D.

[0081] Examples 7 to 9 and Examples 10 and 11 (Comparison)

There were used an o-cresol novolac-type epoxy resin (OCNE; epoxy equivalent: 200, softening point: 65°C) as an epoxy resin component and the StPN-A obtained in Example 1, the StPN-B obtained in Example 2, the StPN-C obtained in Example 3, the StPN-D obtained in Comparative Example 1, and phenol novolac (PN; PSM-4261 (manufactured by Gunee Chemical Industry Co., Ltd.); OH equivalent: 103, softening point: 82°C) as curing agents. Silica (average particle diameter: 18 μm) as a filler and triphenylphosphine as a curing accelerator were kneaded in the composition shown in Table 1 to afford epoxy resin compositions. The epoxy resin compositions were molded at 175°C and were post-cured at 175°C for 12 hours to

prepare cured product specimens. Subsequently, the specimens were subjected to measurement of various physical properties. Details thereof are shown below, and Table 2 shows the results.

[0082] 1) Measurement by gel permeation chromatography (GPC)

An apparatus equipped with TSK gel G4000HXL, TSK gel G3000HXL, and TSK gel G2000HXL, which were manufactured TOSOH CORPORATION, arranged in series was used, and the column temperature was set to 40°C. In addition, tetrahydrofuran was used as an eluent, and measurement was performed at a flow rate of 1 ml/min using an RI (differential refractometer) detector as a detector. 0.1 g of each of the samples was dissolved in 10 ml of THF. A calibration curve based on standard polystyrene was used to determine a weight-average molecular weight (M_w) and a number-average molecular weight (M_n), and then a molecular weight distribution (M_w/M_n) was calculated.

[0083] 2) Softening point

The softening point was measured using an automatic softening point measurement apparatus (manufactured by Meiho, ASP-M4SP) by a ring-and-ball method according to JIS-K-2207.

[0084] 3) Melt viscosity

The melt viscosity was measured at 150°C using a rotating viscosimeter (manufactured by BROOKFIELD, model CAP 2000H).

[0085] 4) Measurement of hydroxy group equivalent

The hydroxy group equivalent was measured with a potentiometric titrator using 1,4-dioxane as a solvent by: performing acetylation with 1.5 mol/L acetyl chloride; decomposing an excessive amount

of acetyl chloride with water; and performing titration with 0.5 mol/L potassium hydroxide.

[0086] 5) Measurement of epoxy equivalent

The epoxy equivalent was measured with a potentiometric titrator using methyl ethyl ketone as a solvent by: adding an acetic acid solution of tetraethylammonium bromide; and performing measurement with a 0.1 mol/L perchloric acid/acetic acid solution in the potentiometric titrator.

[0087] 6) Gel time

The gel time was measured by: adding an epoxy resin composition on a plate of a gelation tester (manufactured by Nisshin Kagaku) heated to 175°C; stirring the composition using a fluororesin bar at a rate of two rotations per second; and determining a gelation time for curing the epoxy resin composition.

[0088] 7) Hot hardness

The hot hardness was measured by: molding a sample at a mold temperature of 175°C for a curing time of 90 seconds; and 10 seconds after mold opening, determining a shore D hardness using a shore D hardness meter.

[0089] 8) Glass transition temperature (T_g), Coefficient of linear thermal expansion (CTE)

A T_g was determined using a thermomechanical measuring apparatus model TMA120C manufactured by Seiko Instruments Inc. under the condition of a temperature increase rate of 10°C/min, an α 1 (CTE equal to or lower than T_g) was determined from an average value

measured in the range of from 30 to 50°C, and an α_2 (CTE equal to or higher than Tg) was determined from an average value measured in the range of from Tg+20°C to Tg+40°C.

[0090] 9) Bending strength and bending elasticity

The bending strength and bending elasticity were measured at normal temperature by a three-point bend test method according to JISK 6911.

[0091] 10) Water absorption rate

The condition of 25°C and 50% relative humidity was defined as a standard state, and a weight change rate was determined after a sample was allowed to absorb moisture for 100 hours under the condition of 85°C and 85% relative humidity.

[0092] 11) Flame retardancy

A specimen having a thickness of 1/16 inch was molded and evaluated based on the UL94 V-0 standard, and the flame retardancy was represented by a total burning time of five specimens.

[0093]

[Table 1]

	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
OCNE	79.6	79.8	81.5	79.4	99.0
StPN-A	70.4	70.2	68.5	70.6	51.0
StPN-B					
StPN-C					
StPN-D					
PN					
Silica	800	800	800	800	800
Curing accelerator	1.2	1.2	1.2	1.2	1.2
Carbon black	5	5	5	5	5
Carnauba wax	3	3	3	3	3
Silica content (wt%)	83	83	83	83	83

[0094]

[Table 2]

	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
Gel time (sec)	38	35	32	45	25
Hot hardness	73	76	80	65	86
Tg (°C)	112	114	110	109	165
CTE (<Tg, $\times 10^{-5}$)	1.1	1.1	1.1	1.1	1.1
CTE (>Tg, $\times 10^{-5}$)	4.4	4.4	4.5	4.5	4.3
Bending strength (MPa)	120	123	118	111	158
Bending elasticity (GPa)	20.5	20.9	20.0	20.2	25.7
Water absorption rate (wt%)	0.23	0.23	0.24	0.23	0.26
Burning time (sec)	47	26	45	98	332

[0095] Examples 12 to 14 and Examples 15 and 16 (Comparison)

There were used the StPNE-A obtained in Example 4, the StPNE-B obtained in Example 5, the StPNE-C obtained in Example 6, the StPNE-D obtained in Comparative Example 2, and an o-cresol novolac-type epoxy resin (OCNE; epoxy equivalent: 200, softening point: 65°C)

as epoxy resin components and a phenol aralkyl resin (PA; MEH-7800SS (manufactured by MEIWA PLASTIC INDUSTRIES, LTD.), OH equivalent: 175, softening point: 67°C) as a curing agent. Further, spherical silica (average particle diameter: 18 µm) as a filler and triphenylphosphine as a curing accelerator were used to afford epoxy resin compositions having the compositions shown in Table 3. The numerical values in the table represent parts by weight in the compositions.

[0096] The epoxy resin compositions were molded at 175°C and was post-cured at 175°C for 12 hours to prepare cured product specimens. Subsequently, the specimens were subjected to measurement of various physical properties. Table 4 shows the results.

[0097]

[Table 3]

	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16
StPNE-A	86.9	87.5	86.1	87.6	80.0
StPNE-B					
StPNE-C					
StPNE-D					
OCNE					
PA	63.1	62.5	63.9	62.4	70.0
Silica	800	800	800	800	800
Curing accelerator	1.2	1.2	1.2	1.2	1.2
Carbon black	5	5	5	5	5
Carnauba wax	3	3	3	3	3
Silica content (wt%)	83	83	83	83	83

[0098]

[Table 4]

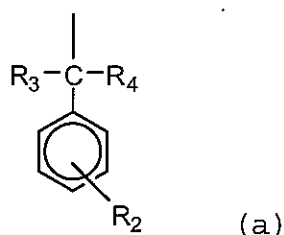
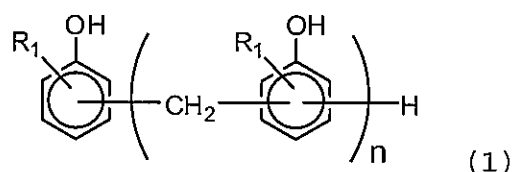
	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Gel time (sec)	39	37	35	48	27
Hot hardness	71	73	78	63	87
Tg (°C)	130	132	128	127	138
CTE (<Tg, $\times 10^{-5}$)	1.1	1.1	1.1	1.1	1.1
CTE (>Tg, $\times 10^{-5}$)	4.9	4.8	5.0	5.1	4.8
Bending strength (MPa)	140	142	140	137	151
Bending elasticity (GPa)	18.0	18.5	17.9	17.8	20.2
Water absorption rate (wt%)	0.22	0.22	0.23	0.22	0.26
Burning time (sec)	43	27	40	65	223

Industrial Applicability

[0099] When the epoxy resin and polyvalent hydroxy resin of the present invention are applied to an epoxy resin composition, the resins are excellent in curability and mechanical physical properties, provides a cured product excellent in flame retardancy, moisture resistance, and low elasticity, and can be suitably used for applications such as sealing of electrical and electronic parts, and circuit board materials. In particular, it is possible to use no or a reduced amount of a flame retardant having an environmental load while maintaining excellent curability and flame retardancy and excellent moldability.

Claims

[Claim 1] An aralkyl-modified polyvalent hydroxy resin, which is obtained by subjecting a polyvalent hydroxy compound represented by the following general formula (1):



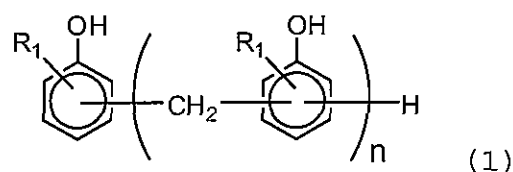
wherein R₁ and R₂ each represent a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, R₃ and R₄ each represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, and n represents a number of from 1 to 5,

to a reaction with an aralkylating agent to substitute a benzene ring in the polyvalent hydroxy compound by an aralkylating agent-derived substituent represented by the formula (a),

the aralkyl-modified polyvalent hydroxy resin being obtained by using, as the polyvalent hydroxy compound represented by the general formula (1), a narrowly dispersed polyvalent hydroxy compound including, in terms of area% measured by gel permeation chromatography, 15% or less of n=1 component and 50% or more of a total of n=2 and n=3 components and having an Mw/Mn of 1.2 or less.

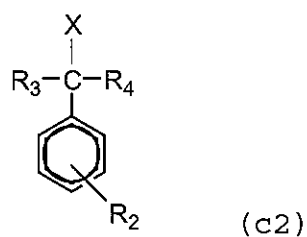
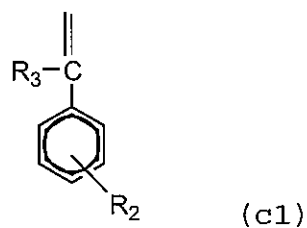
[Claim 2] An aralkyl-modified polyvalent hydroxy resin according to claim 1, wherein the aralkylating agent is styrene.

[Claim 3] A production method for an aralkyl-modified polyvalent hydroxy resin, the production method comprising producing an aralkyl-modified polyvalent hydroxy resin, which is obtained by subjecting a polyvalent hydroxy compound represented by the following general formula (1):



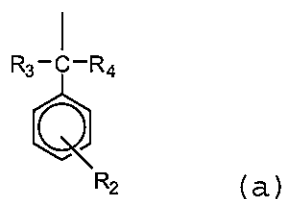
wherein R₁ and R₂ each represent a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, and n represents a number of from 1 to 5,

to a reaction with an aralkylating agent represented by the following formula (c1) or (c2):



wherein R_2 represents a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, R_3 and R_4 each represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, X represents a halogen, OH, or OR_5 , and R_5 represents an alkyl group having 1 to 6 carbon atoms,

to substitute a benzene ring in the polyvalent hydroxy compound by an aralkylating agent-derived substituent represented by the formula (a):



wherein R_2 , R_3 , and R_4 have the same meanings as those defined for the formulae (c1) and (c2),

using as the polyvalent hydroxy compound represented by the general formula (1), a narrowly dispersed polyvalent hydroxy compound including, in terms of area% measured by gel permeation chromatography, 15% or less of $n=1$ component and 50% or more of a total of $n=2$ and $n=3$ components and having an M_w/M_n of 1.2 or less,

the reaction being performed in a presence of from 10 to 1,000 ppm of an acid catalyst at a reaction temperature of from 40 to 120°C.

[Claim 4] A production method for an aralkyl-modified polyvalent hydroxy resin according to claim 3, wherein the reaction comprises

subjecting from 0.1 to 1.5 mol of the aralkylating agent to a reaction with 1 mol of a hydroxy group in the polyvalent hydroxy compound.

[Claim 5] A production method for an aralkyl-modified polyvalent hydroxy resin according to claim 3, wherein the aralkylating agent is styrene.

[Claim 6] An epoxy resin composition, comprising an epoxy resin and a curing agent, the epoxy resin composition being obtained by using, as a part or whole of the curing agent, the aralkyl-modified polyvalent hydroxy resin according to claim 1 as an essential component.

[Claim 7] An epoxy resin cured product, which is obtained by curing the epoxy resin composition according to claim 6.

[Claim 8] An epoxy resin, which is obtained by subjecting the aralkyl-modified polyvalent hydroxy resin according to claim 1 to a reaction with epichlorohydrin.

[Claim 9] A production method for an epoxy resin, the production method comprising subjecting the aralkyl-modified polyvalent hydroxy resin according to claim 1 to a reaction with epichlorohydrin to convert a hydroxy group in the aralkyl-modified polyvalent hydroxy resin into a glycidyl ether group.

[Claim 10] An epoxy resin composition, comprising an epoxy resin and a curing agent, the epoxy resin composition being obtained by blending the epoxy resin according to claim 8 as an essential component.

[Claim 11] An epoxy resin cured product, which is obtained by curing the epoxy resin composition according to claim 10.