

S P E C I F I C A T I O N

Title of the Invention

Polyhydric Hydroxy Resin, Epoxy Resin, Production Method Thereof, Epoxy Resin Composition, and Cured Product Thereof

Technical Field

[0001] This invention relates to an epoxy resin that has excellent curing properties and yields a cured product of excellent flame retardancy, excellent moisture resistance, and low elasticity, a polyhydric hydroxy resin that is suitable as an intermediate of the epoxy resin, the methods of producing these resins, an epoxy resin composition comprising these resins, and a cured product of the epoxy resin composition. The epoxy resin composition is suitable for use as an encapsulating material of semiconductors and an insulating material of printed circuit boards and the like in the electric and electronic fields.

Background Technology

[0002] Epoxy resins have been used industrially in a wide variety of applications and, in recent years, the requirements for their performance are becoming increasingly sophisticated. For example, a typical area of application for resins that are mainly composed of epoxy resins is an encapsulating material of semiconductors. As the degree of integration of a semiconductor device increases, the package is becoming larger in area and smaller in thickness and, at the same time, the packaging process is undergoing a transfer to surface mount technology. This has created a demand for development of a material of excellent

solder heat resistance. In consequence, there is a demand for an encapsulating material that is reduced in moisture absorption and improved in adhesiveness at the interface with a material of different kind such as a lead frame and a chip. The situation is the same for a printed circuit board material and there is a demand for development of a material that is reduced in moisture absorption and improved in heat resistance and adhesiveness from the viewpoint of improving the solder heat resistance and is additionally provided with low dielectric properties from the viewpoint of reducing dielectric loss. To meet these demands, epoxy resins with a variety of novel structures and curing agents thereof have been investigated. Moreover, the recent trend is to eliminate halogen-based flame retardants from the viewpoint of reducing environmental load and this has created a demand for epoxy resins and curing agents with improved flame retardancy.

[0003] Under the aforementioned circumstances, a variety of epoxy resins and curing agents thereof have been investigated. An example of known epoxy resin curing agents is a naphthalene-based resin. Patent document 1 describes an application of a naphthol aralkyl resin as an encapsulating material of semiconductors and further describes good flame retardancy, low moisture absorption, and low thermal expansion of the resin. Meanwhile, patent document 2 proposes a curing agent of biphenyl structure and describes that the curing agent is effective for improving flame retardancy. However, both the naphthol aralkyl resin and the biphenyl aralkyl resin have shortcomings in curing properties and, in some cases, they are not sufficiently effective for improving flame retardancy.

[0004] On the other hand, like the curing agents described above, none of known epoxy resins satisfies the aforementioned requirements. For example, commonly known epoxy resins of bisphenol type are liquid at ambient temperature and, although they enjoy wide usage because they are easy to work with and can be readily mixed with curing agents, additives,

and the like, they present problems in heat resistance and moisture resistance. Epoxy resins of o-cresol novolac type are known for improved heat resistance, but they perform insufficiently in flame retardancy.

[0005] Addition of a phosphate ester-based flame retardant is disclosed as a means to improve flame retardancy without using a halogen-based flame retardant. However, the use of a phosphate ester-based flame retardant does not provide sufficient moisture resistance. Furthermore, a phosphate ester undergoes hydrolysis in an environment of high temperature and high humidity thereby presenting a problem of degrading reliability as an insulating material.

[0006] Regarding a means to improve flame retardancy without incorporating phosphorus or halogen atoms, patent documents 2 and 3 disclose applications of aralkyl type epoxy resins of biphenyl structure as encapsulating materials of semiconductors. Patent document 4 discloses the use of an aralkyl type epoxy resin of naphthalene structure. However, these epoxy resins do not perform sufficiently in either of flame retardancy, moisture resistance, and heat resistance.

[0007] On the other hand, patent document 5 discloses benzylated polyphenols and epoxy resins derived therefrom as examples of substances developed with a focus on improvement of heat resistance, moisture resistance, and crack resistance, but not on improvement of flame retardancy. The epoxy resin in question is obtained by using a phenol novolac as a starting material and subjecting it to addition reaction with benzyl chloride. However, the reaction is carried out under a strongly acidic condition wherein hydrochloric acid generated in the reaction is utilized as a catalyst and, as a result, the methylene linkages in the phenol novolac partly rupture to produce phenol as a by-product. That is, the problem encountered here is

that incorporation of the by-product monofunctional phenol in the resin leads to deterioration of curing properties and heat resistance.

[0008] Further, patent document 6 discloses the reaction of a phenol novolac with a styrene in the presence of an acid catalyst as an example of methods for producing a styrene-modified novolac. As this reaction uses strongly acidic sulfuric acid as a catalyst at high temperatures, the same problem as above occurs here because the methylene linkages in the phenol novolac partly rupture to produce a phenol as a by-product.

[0009] On the other hand, as examples of epoxy resin compositions developed with a focus on improvement of moisture resistance and reduction of stress, patent documents 7 and 8 disclose epoxy resin compositions using styrenated phenol novolac resins and epoxy resins derived therefrom, but neither of these resins is developed with a focus on improvement of flame retardancy. Moreover, since the method employed comprises using a styrenated phenol as a starting material and converting it to a novolac, the styrenated phenol which is a high-boiling substance remains in the resin thereby causing a problem of deteriorating curing properties and heat resistance.

Prior Art Technical Documents

Patent Documents

[0010] Patent document 1: JP2005-344081 A

Patent document 2: JP H11-140166 A

Patent document 3: JP2000-129092 A

Patent document 4: JP2004-59792 A

Patent document 5: JP H08-120039 A

Patent document 6: JP S48-52895 A

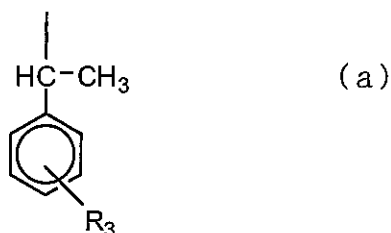
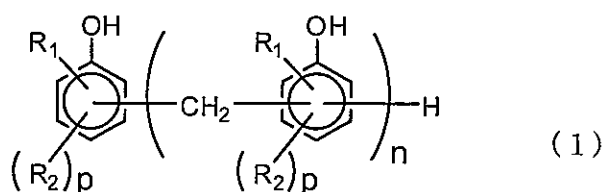
Patent document 7: JP H05-132544 A

Patent document 8: JP H05-140265 A

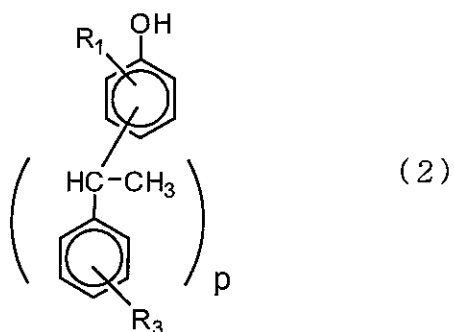
Summary of the Invention

[0011] An object of this invention is to provide an epoxy resin that has excellent curing properties and performs with excellent flame retardancy, excellent moisture resistance, and low dielectric properties in applications such as lamination, molding, casting, adhesion, and the like, to provide an epoxy resin composition that has excellent curing properties and yields a cured product of excellent flame retardancy, excellent moisture resistance, and low dielectric properties and is useful as a material for encapsulating electric and electronic parts and as a circuit board material, and to provide a cured product of the said epoxy resin composition.

[0012] Accordingly, this invention relates to a polyhydric hydroxy resin represented by the following general formula (1) wherein a monohydric hydroxy compound represented by the following general formula (2) accounts for 3% or less by area when detected by gel permeation chromatography (GPC, RI detector).

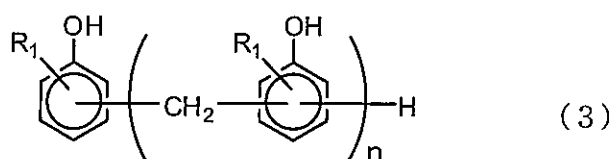


(R₁ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms; R₂ is a substituent represented by the following formula (a); n is a number of 0 to 20; p is a number of 0.1 to 2.5; and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms.)

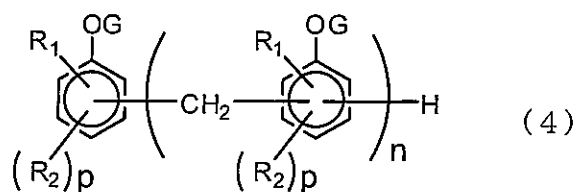


(Here, p is a number of 0 to 3 and each of R₁ and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms.)

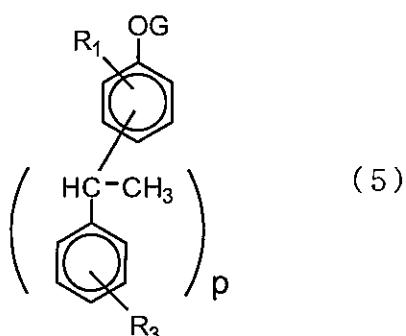
[0013] Further, this invention relates to a method for producing a polyhydric hydroxy resin that comprises reacting a polyhydric hydroxy compound represented by the following general formula (3) with a styrene at a ratio of 1 mole of the hydroxyl group of the polyhydric hydroxy compound to 0.1 to 1.0 mole of the styrene in the presence of 10 to 400 wt ppm of an acid catalyst at a reaction temperature of 40 to 120°C to introduce a substituent represented by the aforementioned formula (a) to the benzene rings of the polyhydric hydroxy compound.



[0014] Further, this invention relates to an epoxy resin represented by the following general formula (4) wherein a monofunctional epoxy resin represented by the following general formula (5) accounts for 3% or less by area when detected by gel permeation chromatography (GPC, RI detector).



(Here, G is a glycidyl group; R₁ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms; R₂ is a substituent represented by the aforementioned formula (a); R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms; n is a number of 1 to 20; and p is a number of 0.1 to 2.5.)



(Here, G is a glycidyl group; each of R₁ and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms; p is a number of 0 to 3.)

[0015] Further, this invention relates to a method for producing an epoxy resin that comprises reacting the aforementioned polyhydric hydroxy resin with epichlorohydrin.

[0016] Still further, this invention relates to an epoxy resin composition comprising an epoxy resin and a curing agent wherein one or both of the aforementioned polyhydric hydroxy resin and the aforementioned epoxy resin are incorporated as an essential component. In addition, this invention relates to a cured product of epoxy resin produced by curing the aforementioned epoxy resin composition.

Brief Description of the Drawings

[0017]

Fig. 1 is a GPC chart of the polyhydric hydroxy resin obtained in Example.

Fig. 2 is a GPC chart of the polyhydric hydroxy resin obtained in Synthetic Example.

Fig. 3 is a GPC chart of the epoxy resin obtained in Example.

Fig. 4 is a GPC chart of the epoxy resin obtained in Synthetic Example.

Preferred Embodiments of the Invention

[0018] First, the polyhydric hydroxy resin of this invention (hereinafter referred to as StPN) is explained. StPN of this invention is represented by general formula (1) and it can be produced by reacting a polyhydric hydroxy compound (hereinafter also referred to as polyhydric hydroxy compound (3)) with a styrene.

[0019] Addition of a styrene to a polyhydric hydroxy compound is generally effected by carrying out the reaction in the presence of an acid catalyst such as hydrochloric acid at high temperatures in the range of 120 to 170°C. However, when the reaction is carried out in the presence of an acid catalyst at high temperatures, there arises a problem that the reaction is accompanied by cleavage of the methylene linking groups in the polyhydric hydroxy compound and a monohydric phenol is produced as a by-product. It is possible to suppress a secondary reaction such as this and reduce the formation of the by-product monohydric phenol by dropping the reaction temperature to within the range of 40 to 120°C and reducing the amount of catalyst to within the range of 10 to 400 ppm. A polyhydric hydroxy compound produced in this manner manifests excellent curing properties and heat resistance when used as a curing agent for epoxy resins.

[0020] The content of the monohydric hydroxy compound produced by a secondary reaction and represented by the aforementioned general formula (2) (hereinafter also referred to as monohydric hydroxy compound (2)) in the polyhydric hydroxy resin component is preferably 3% or less by area when detected by gel permeation chromatography (GPC, RI detector). When the content is higher than this, the by-product monohydric hydroxy compound tends to deteriorate the curing properties of the polyhydric hydroxy resin when the resin is used as a curing agent for epoxy resins. Furthermore, the monohydric hydroxy compound tends to lower the crosslink density of cured epoxy resin thereby deteriorating heat resistance.

[0021] The polyhydric hydroxy resin contains a styrene oligomer as a by-product in addition to the monohydric hydroxy compound. This oligomer is produced as a by-product in the polymerization reaction of a styrene itself and, in particular, it is contained as a low molecular weight component. Like the monohydric hydroxy compound, the styrene oligomer tends to deteriorate curing properties and heat resistance.

[0022] In a cured product of epoxy resin, a hydroxypropyl group formed by the reaction of an epoxy group with a hydroxyl group is said to be inflammable. However, addition of a styrene to a polyhydric hydroxy compound in order to enhance the hydroxyl equivalent reduces the proportion of aliphatic carbon in the inflammable component derived from an epoxy group and enables the cured product to manifest a high degree of flame retardancy. Further, addition of a highly aromatic styrene intensifies the aromatic property of a polyhydric hydroxy resin and is effective for improving moisture resistance as well as flame retardancy.

[0023] Thus, the aforementioned materials afford highly flame-retardant epoxy resin compositions, particularly suitable for use in encapsulation of semiconductors. That is, the

compositions have excellent curing properties and, at the same time, manifest excellent flame retardancy and moisture resistance and low elasticity. The use of these materials affords highly reliable encapsulating materials for electric and electronic parts and materials for circuit boards.

[0024] StPN of this invention can be produced by the addition reaction of polyhydric hydroxy compound (3) represented by general formula (3) and a styrene. As to the ratio of the two in this reaction, the styrene is preferably in the range of 0.1 to 2.5 moles, more preferably in the range of 0.1 to 1.0 mole, still more preferably in the range of 0.3 to 0.8 mole, per 1 mole of polyhydric hydroxy compound (3) in consideration of the balance of the flame retardancy of the cured product to be produced and the curing properties of the materials to be cured. In the case where the styrene is used in an amount smaller than the aforementioned range, the properties of the raw material polyhydric hydroxy compound remain unimproved. In the case where the styrene is used in excess of the aforementioned range, there is a tendency that the density of functional groups becomes too low and the curing properties deteriorate.

[0025] In the aforementioned reaction, the styrene adds to an aromatic ring containing an OH group in polyhydric hydroxy compound (3), that is, substitution of a styrenyl group represented by the aforementioned formula (a) takes place. The styrene adds to the ortho and/or para position where it is free of a substituent, mainly to the para position, in the polyhydric hydroxy compound.

[0026] The melt viscosity of StPN of this invention at 150°C is preferably in the range of 0.01 to 10.0 Pa · s. For ease of working, the melt viscosity is lower the better in the aforementioned range.

[0027] The softening point is in the range of 40 to 150°C, preferably in the range of 50 to 100°C. The softening point as used here means the softening point determined by the ring and ball method according to JIS-K-2207. When StPN having a softening point lower than this is incorporated in an epoxy resin, the heat resistance of the cured product deteriorates. When the softening point is higher than this, the flow properties during molding deteriorate.

[0028] The symbol R_2 is a styrenyl group represented by the aforementioned formula (a). The symbol p is a number of 0.1 to 2.5 and means the average number (number average) of styrenyl groups introduced to one phenol ring; p is preferably 0.1 to 2, more preferably 0.1 to 1.0, still more preferably 0.3 to 1, most preferably 0.3 to 0.8. Since the phenol rings at both ends can be substituted with a maximum of 4 styrenyl groups and the intermediate phenol rings can be substituted with a maximum of 3 styrenyl groups, StPN can be substituted with a maximum of 8 styrenyl groups when n is 1.

From another point of view, the number of substituted styrenyl groups per one molecule (number average) of StPN of this invention is preferably 1 or more, more preferably 2 or more, still more preferably 2.6 to 4.

[0029] In formula (a), R_3 is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms, preferably a hydrogen atom or an alkyl group of 1 to 3 carbon atoms, still more preferably a hydrogen atom. What is R_3 is decided by a styrene to be used as a raw material in the reaction.

[0030] In general formula (1), n is a number of 1 to 20 and the mean of n is preferably in the range of 1.5 to 5.0.

[0031] Next, the method for producing StPN of this invention is explained. A phenol novolac is

used as polyhydric hydroxy compound (3) according to this invention.

[0032] A phenol to be used in the production of this polyhydric hydroxy compound (3) is phenol or phenol substituted with a hydrocarbon group of 1 to 6 carbon atoms and examples of phenol substituted with a hydrocarbon group include cresols, ethylphenols, isopropylphenols, tert-butylphenols, allylphenols, and phenylphenols. Of these phenols, phenol or phenol substituted with an alkyl group of 1 to 3 carbon atoms is preferred and phenol is more preferred.

A phenol may contain a small amount of other phenolic components. For example, in the case where phenol is used, examples of other phenolic components include o-cresol, m-cresol, p-cresol, ethylphenols, isopropylphenols, tert-butylphenols, allylphenols, phenylphenols, 2,6-xylenol, 2,6-diethylphenol, hydroquinone, resorcin, catechol, 1-naphthol, 2-naphthol, 1,5-naphthalenediol, 1,6-naphthalenediol, 1,7-naphthalenediol, 2,6-naphthalenediol, and 2,7-naphthalenediol. These phenols or naphthols may be a mixture of two kinds or more.

[0033] A styrene to be used in the reaction with a polyhydric hydroxy compound is styrene or styrene substituted with a hydrocarbon group of 1 to 6 carbon atoms. These styrenes may contain a small amount of other reaction components. In the case where such other reaction component is a compound containing an unsaturated linkage like α -methylstyrene, divinylbenzene, indene, coumarone, benzothiophene, indole, or vinyl naphthalene, the product polyhydric hydroxy compound is bound to have a group generated by such a compound as a substituent on its aromatic rings. A phenol resin to be produced by the method of this invention for producing a polyhydric hydroxy resin may contain a polyhydric hydroxy resins carrying such substituents. Likewise, an epoxy resin to be produced by the method of this invention for producing an epoxy resin may contain an epoxy resin carrying such substituents.

[0034] This reaction may be carried out in the presence of an acid catalyst and the amount of the catalyst is in the range of 10 to 400 ppm, preferably in the range of 100 to 350 ppm. When the amount exceeds this range, the methylene linkages of phenol novolac tends to be cleaved easily and a monohydric phenol produced as a by-product of the cleavage deteriorates curing properties and heat resistance. On the other hand, when the amount is below this range, the reactivity of the styrene drops and a large amount of the styrene monomer remains unreacted. The amount of the catalyst used here means the amount used against the total weight of the raw material polyhydric hydroxy compound and styrene.

[0035] This reaction may be carried out in the presence of an acid catalyst. The acid catalyst may be selected suitably from known inorganic and organic acids. Specific examples include mineral acids such as hydrochloric acid, sulfuric acid, and phosphoric acid, organic acids such as formic acid, oxalic acid, trifluoroacetic acid, o-toluenesulfonic acid, dimethylsulfuric acid, and diethylsulfuric acid, Lewis acids such as zinc chloride, aluminum chloride, iron chloride, and boron trifluoride, and solid acids such as ion exchange resin, activated clay, silica-alumina, and zeolite.

[0036] The reaction is carried out at a temperature in the range of 40 to 120°C. At a temperature below this range, the reactivity drops and the reaction time becomes longer. On the other hand, at a temperature above this range, partial cleavage of the methylene linkages of phenol novolac tends to occur easily and a monohydric phenol produced as a by-product of the cleavage deteriorates curing properties and heat resistance.

[0037] The reaction is normally carried out for a period of 1 to 20 hours. A solvent may be used in the reaction and specific examples include alcohols such as methanol, ethanol, propanol,

butanol, ethylene glycol, methyl cellosolve, and ethyl cellosolve, ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, ethers such as dimethyl ether, diethyl ether, diisopropyl ether, tetrahydrofuran, and dioxane, and aromatic compounds such as benzene, toluene, chlorobenzene, and dichlorobenzene.

[0038] A concrete procedure generally used to effect this reaction comprises either introducing the whole raw materials together and allowing them to react at a prescribed temperature or introducing a polyhydric hydroxy compound and a catalyst first, keeping them at a prescribed temperature, and adding dropwise a styrene. In the case of dropwise addition, the period therefor is normally 1 to 10 hours, preferably 5 hours or less. Upon completion of the reaction, the resin of this invention is obtained by removing the catalyst if necessary and distilling off a solvent when it is used or the target product is obtained by directly discharging while hot when a solvent is not used.

[0039] Next, the epoxy resin of this invention is described

The epoxy resin of this invention (abbreviated as StPNE) is represented by general formula (4). The polyhydric hydroxy resin (StPN) is represented by general formula (1). StPNE can be produced by epoxidizing StPN.

[0040] In general formulas (1) and (4), the symbols commonly used therein have the same meaning. The symbol G is a glycidyl group and formed by the reaction of the hydroxyl group in general formula (1). The symbol R₁ is a styrenyl group.

[0041] StPNE of this invention is advantageously produced by the reaction of StPN represented by the aforementioned general formula (1) with epichlorohydrin, but it may be produced otherwise. However, a care is exercised so that StPN does not contain more than 3%

of the aforementioned monohydric hydroxy compound. In this manner, the content of a monofunctional epoxy resin represented by the aforementioned general formula (5) (hereinafter also referred to as monofunctional epoxy resin (5)) in StPNE can be maintained below 3%.

[0042] Besides the reaction of StPN with epichlorohydrin, it is possible to adopt a method that comprises reacting StPN with an allyl halide to form an allyl ether compound and then reacting the allyl ether compound with a peroxide. The aforementioned reaction of StPN with epichlorohydrin can be carried out in the same manner as ordinary epoxidation reaction.

[0043] For example, the aforementioned StPN is dissolved in an excess of epichlorohydrin and the solution is allowed to react in the presence of an alkali metal hydroxide such as sodium hydroxide and potassium hydroxide at a temperature in the range of 20 to 150°C, preferably in the range of 30 to 80°C, for a period of 1 to 10 hours. The amount of the alkali metal hydroxide to be used here is in the range of 0.8 to 1.5 moles, preferably in the range of 0.9 to 1.2 moles, per 1 mole of the hydroxyl group of StPN. Further, although epichlorohydrin is used in excess of 1 mole of the hydroxyl group of StPN, it is normally used in an amount in the range of 1.5 to 30 moles, preferably in the range of 2 to 15 moles, per 1 mole of the hydroxyl group of StPN. Upon completion of the reaction, the excess epichlorohydrin is distilled off, the residue is dissolved in a solvent such as toluene and methyl isobutyl ketone, the solution is filtered, and the filtrate is washed with water to remove inorganic salts and stripped of the solvent by distillation to yield the target epoxy resin.

[0044] The epoxy resin composition of this invention comprises at least an epoxy resin and a curing agent and there are the following three kinds.

1) A composition in which the aforementioned StPNE is incorporated as a part or the whole of

the epoxy resin.

2) A composition in which the aforementioned StPN is incorporated as a part or the whole of the curing agent.

3) A composition in which the aforementioned StPNE and StPN are incorporated respectively as a part or the whole of the epoxy resin and the curing agent.

[0045] The compositions described in 2) and 3) above respectively contain StPN as an essential component. The amount of StPN to be incorporated is normally in the range of 2 to 200 parts by weight, preferably in the range of 5 to 80 parts by weight, per 100 parts by weight of the epoxy resin. An amount smaller than this produces a poor effect for improving flame retardancy and moisture absorption while an amount larger than this causes a problem of deteriorating the curing properties of the epoxy resin composition and the strength of the cured product.

[0046] In the case where StPN is used as the whole of the curing agent, the amount of StPN to be incorporated is normally decided in consideration of the balance between the hydroxyl equivalent of StPN and the epoxy equivalent of the epoxy resin. The equivalent ratio of the epoxy resin to the curing agent is normally in the range of 0.2 to 5.0, preferably in the range of 0.5 to 2.0. When the equivalent ratio is either larger or smaller than this, the curing properties of the epoxy resin composition deteriorate and the heat resistance, mechanical strength, and the like of the cured product deteriorate as well.

[0047] Other curing agent may be used together with StPN. The amount of such other curing agent to be incorporated is normally decided in such a range as to maintain the amount of incorporated StPN in the range of 2 to 200 parts by weight, preferably in the range of 5 to 80 parts by weight, per 100 parts by weight of the epoxy resin. When the amount of incorporated

StPN is smaller than this, a poor effect is produced for reducing moisture absorption and improving adhesiveness and flame retardancy. When the amount of incorporated StPN is larger than this, there arises a problem of deterioration of the curing properties and the strength of the cured product. In this case as well, the equivalent ratio of the epoxy resin to the combined curing agents is kept in the aforementioned range.

[0048] As a curing agent other than StPN, any material generally known as a curing agent for epoxy resins can be used and examples include dicyandiamide, acid anhydrides, polyhydric phenols, and aromatic and aliphatic amines. Of these compounds, polyhydric phenols are preferably used as curing agents in the areas such as encapsulation of semiconductors where a high degree of electrical insulation is required. Specific examples of curing agents are described below.

[0049] Specific examples of the acid anhydrides include phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methyl himic anhydride, dodecylsuccinic anhydride, nadic anhydride, and trimellitic anhydride.

[0050] Specific examples of the polyhydric phenols include dihydric phenols such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, and naphthalenediol and trihydric or higher phenols such as tris(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, o-cresol novolac, naphthol novolac, and polyvinylphenol. The examples further include polyhydric phenol compounds 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, and naphthalenediol and a condensing agent such as formaldehyde,

acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, p-xylylene dichloride, bischloromethylbiphenyl, and bischloromethylnaphthalene.

[0051] Specific examples of the amines include aromatic amines such as 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenyl sulfone, m-phenylenediamine, and p-xylylenediamine and aliphatic amines such as ethylenediamine, hexamethylenediamine, diethylenetriamine, and triethylenetetramine.

One kind or a mixture of two kinds or more of these curing agents may be used in the aforementioned composition.

[0052] The epoxy resin to be used in the aforementioned composition is selected from compounds containing two or more epoxy groups in the molecule. Examples of such compounds include epoxides of dihydric phenols such as bisphenol A, bisphenol F, 3,3',5,5'-tetramethylbisphenol F, bisphenol S, fluorenebisphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenol, resorcin, and a naphthalenediol, epoxides of trihydric or higher phenols such as tris(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, and o-cresol novolac, epoxides of resins obtained by copolycondensation of dicyclopentadiene and phenols, epoxides of biphenyl aralkyl type phenolic resins synthesized from phenols and bischloromethylbiphenyl, and epoxides of naphthol aralkyl resins synthesized from naphthols and p-xylylene dichloride. These epoxy resins may be used singly or as a mixture of two kinds or more.

[0053] The composition described in 1) or 3) above comprises StPNE as an essential component. It is allowable to incorporate an epoxy resin, different in kind from StPNE, in this epoxy resin composition. In this case, any of ordinary epoxy resins containing two or more epoxy groups in the molecule may be used. Specific examples include glycidyl ethers derived

from dihydric phenols such as bisphenol A, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, and resorcin, trihydric or higher phenols such as tris(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, and o-cresol novolac, phenol aralkyl resins, biphenyl aralkyl resins, naphthol aralkyl resins, and halogenated bisphenols such as tetrabromobisphenol A. These epoxy resins may be used singly or as a mixture of two kinds or more. In the case where the composition comprises StPNE of this invention as an essential component, the amount of StPNE to be incorporated is in the range of 5 to 100%, preferably in the range of 60 to 100%, of the whole epoxy resin.

[0054] It is allowable to incorporate suitably an oligomer or high molecular weight compound such as polyester, polyamide, polyimide, polyether, polyurethane, petroleum resin, indene resin, indene • coumarone resin, and phenoxy resin as a modifier or the like in the epoxy resin composition of this invention. The amount to be incorporated is normally in the range of 2 to 30 parts by weight per 100 parts by weight of the epoxy resin.

[0055] Further, it is allowable to incorporate an additive such as inorganic filler, pigment, flame retardant, thixotropic agent, coupling agent, and flowability improver in the epoxy resin composition of this invention. Example of the inorganic filler include silica powder such as spherical or crushed fused silica and crystalline silica, alumina powder, glass powder, mica, talc, calcium carbonate, alumina, and hydrated alumina. When used in an encapsulating material for semiconductors, the amount of the filler to be incorporated is preferably 70 wt% or more, more preferably 80 wt% or more.

[0056] Examples of the pigment include organic or inorganic extender pigments and scaly pigments. Examples of the thixotropic agent include materials based on silicone, castor oil, aliphatic amide wax, oxidized polyethylene wax, and organic bentonite.

[0057] Further, it is allowable to use a curing accelerator in the epoxy resin composition of this invention if necessary. Examples of the curing accelerator includes amines, imidazoles, organic phosphines, Lewis acids, and the like; specifically, tertiary amines such as 1,8-diazabicyclo(5,4,0)undecene-7, triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, and tris(dimethylaminomethyl)phenol, imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 2-phenyl-4-methylimidazole, and 2-heptadecylimidazole, organic phosphines such as tributylphosphine, methyldiphenylphosphine, triphenylphosphine, diphenylphosphine, and phenylphosphine, tetra-substituted phosphonium tetra-substituted borates such as tetraphenylphosphonium tetraphenylborate, tetraphenylphosphonium ethyltriphenylborate, and tetrabutylphosphonium tetrabutylborate, and tetraphenylboron salts such as 2-ethyl-4-methylimidazole tetraphenylborate and N-methylmorpholine tetraphenylborate. The amount of the curing accelerator to be added is normally in the range of 0.2 to 5 parts by weight per 100 parts by weight of the epoxy resin.

[0058] If necessary, it is further allowable to use a mold release agent such as canauba wax and OP wax, a coupling agent such as γ -glycidoxypyriltrimethoxysilane, a colorant such as carbon black, a flame retardant such as antimony trioxide, a stress reducing agent such as silicone oil, and a lubricant such as calcium stearate in the epoxy resin composition of this invention.

[0059] The epoxy resin composition of this invention can be converted to a prepreg by dissolving the composition in an organic solvent to a state of varnish, impregnating a fibrous material such as glass cloth, aramid nonwoven fabric, and liquid crystalline polyester nonwoven fabric with the varnish, and removing the solvent. According to circumstances, the

composition is made into a laminate by coating a sheet-like material such as copper foil, stainless steel foil, polyimide film, and polyester film with a solution of the composition.

[0060] The epoxy resin composition of this invention yields a cured product when cured by heating. The composition has excellent curing properties and the cured product has excellent flame retardancy, low moisture absorption, and low elasticity. The cured product can be processed by a molding technique such as casting, compression molding, and transfer molding. The molding temperature is normally in the range of 120 to 220°C.

Examples

[0061] This invention is explained in more detail below with reference to the examples.

[0062]

(Synthesis of polyhydric hydroxy resin)

Example 1

In a 1-L four-necked flask were placed 105 g of a phenol novolac (BRG-555 manufactured by Showa Highpolymer Co., Ltd; hydroxyl equivalent 105 g/eq., softening point 67°C, melt viscosity at 150°C 0.08 Pa · s) as a polyhydric hydroxy compound component, 5.3 g of toluene, and 0.078 g (300 ppm) of p-toluenesulfonic acid as an acid catalyst and the mixture was heated to 100°C. Then, 156 g (1.5 mol) of styrene was added dropwise to the mixture at 100°C with stirring over 3 hours while allowing the reaction to proceed. The reaction was continued for additional 2 hours at 100°C and 0.071 g of 30% Na₂CO₃ was added to neutralize the reaction mixture. The mixture was then dissolved in 485 g of MIBK and the solution was washed 5 times with water at 80°C. Then, the MIBK was distilled off under reduced pressure and a polyhydric hydroxy resin weighing 250 g was obtained. The polyhydric hydroxy resin

had a hydroxyl equivalent of 261 g/eq., a softening point of 82°C, and a melt viscosity at 150°C of 0.21 Pa · s. This resin is referred to as StPN-A. A measurement by gel permeation chromatography (GPC, RI detector) indicated that monohydric hydroxy compound (2) accounts for 1.2% by area. The GPC chart of StPN-A is shown in Fig. 1.

[0063]

Synthetic Example 1

In a 1-L four-necked flask were placed 105 g of a phenol novolac (BRG-555 manufactured by Showa Highpolymer Co., Ltd) as a polyhydric hydroxy compound component, 5.3 g of toluene, and 0.131 g (500 ppm) of p-toluenesulfonic acid as an acid catalyst and the mixture was heated to 150°C. Then, 156 g (1.5 mol) of styrene was added dropwise to the mixture at 150°C with stirring over 3 hours while allowing the reaction to proceed. The reaction was continued for additional 2 hours at 150°C and 0.118 g of 30% Na₂CO₃ was added to neutralize the reaction mixture. The mixture was then dissolved in 485 g of MIBK and the solution was washed 5 times with water at 80°C. Then, the MIBK was distilled off under reduced pressure and a polyhydric hydroxy resin weighing 247 g was obtained. The polyhydric hydroxy resin had a softening point of 80°C, a melt viscosity at 150°C of 0.19 Pa · s, and a hydroxyl equivalent of 261 g/eq. This resin is referred to as StPN-B. A measurement by gel permeation chromatography (GPC, RI detector) indicated that monohydric hydroxy compound (2) accounts for 5.2% by area and a styrene dimer accounts for 0.8% by area. The GPC chart of StPN-B is shown in Fig. 2. In Figs. 1 and 2, A is the peak of monohydric hydroxy compound (2) while B is the peak of the styrene dimer.

[0064]

(Synthesis of epoxy resin)

Example 2

In a four-necked separable flask were placed 150 g of StPN-A obtained in Example 1, 319 g of epichlorohydrin, and 48 g of diethylene glycol dimethyl ether and the mixture was stirred to effect dissolution. After uniform dissolution occurred, the solution was maintained at 65°C under a reduced pressure of 130 mmHg and 47.9 g of a 48% aqueous solution of sodium hydroxide was added dropwise over 4 hours. The reaction was effected under reflux conditions and the water and epichlorohydrin distilling out during the dropwise addition were separated in a separation tank while returning the epichlorohydrin to the reaction vessel and withdrawing the water from the system. Upon completion of the reaction, the salt formed was removed by filtration and the filtrate was further washed with water and stripped of the epichlorohydrin by distillation to give an epoxy resin (StPNE-A) weighing 172 g. The epoxy resin had an epoxy equivalent of 325 g/eq., a softening point of 60°C, and a melt viscosity at 150°C of 0.19 Pa · s. A measurement by gel permeation chromatography (GPC, RI detector) indicated that monofunctional epoxy compound (5) accounts for 1.1% by area. The GPC chart of StPNE-A is shown in Fig. 3.

[0065]

Synthetic Example 2

In a four-necked separable flask were placed 150 g of StPN-B obtained in Synthetic Example 1, 319 g of epichlorohydrin, and 48 g of diethylene glycol dimethyl ether and the mixture was stirred to effect dissolution. After uniform dissolution occurred, the solution was maintained at 65°C under a reduced pressure of 130 mmHg and 47.9 g of a 48% aqueous solution of sodium hydroxide was added dropwise over 4 hours. The reaction was effected under reflux conditions and the water and epichlorohydrin distilling out during the dropwise addition were separated in a separation tank while returning the epichlorohydrin to the reaction vessel and withdrawing the water from the system. Upon completion of the reaction, the salt formed was removed by filtration and the filtrate was further washed with water and

stripped of the epichlorohydrin by distillation to give an epoxy resin (StPNE-B) weighing 170 g. The epoxy resin had an epoxy equivalent of 330 g/eq., a softening point of 57°C, and a melt viscosity at 150°C of 0.18 Pa · s. A measurement by gel permeation chromatography (GPC, RI detector) indicated that monofunctional epoxy compound (5) accounts for 5.0% by area and a styrene dimer accounts for 0.6% by area. The GPC chart of StPNE-B is shown in Fig. 4. In Figs. 3 and 4, A is the peak of monofunctional epoxy compound (5) while B is the peak of the styrene dimer.

[0066]

Example 3 and Comparative Examples 1 and 2

In these examples, an o-cresol novolac type epoxy resin (OCNE: epoxy equivalent 200, softening point 65°C) was used as an epoxy resin component and StPN-A obtained in Example 1, StPN-B obtained in Synthetic Example 1, and a phenol novolac (PN: PSM-4261 manufactured by Gun Ei Chemical Industry Co., Ltd.; OH equivalent 103, softening point 82°C) were used as curing agents. The epoxy resin and the curing agent were compounded with silica (average particle diameter 18 μ m) as a filler, triphenylphosphine as a curing accelerator, and other additives according to the recipe shown in Table 1 to formulate an epoxy resin composition. This epoxy resin composition was molded at 175°C and post-cured at 175°C for 12 hours to yield a cured product and test pieces were prepared from the cured product and tested for a variety of properties. The methods for testing the properties are described in detail below and the results are shown in Table 2.

[0067]

1) Molecular weight distribution of polyhydric hydroxy resin and epoxy resin

The measurement was made with an apparatus for GPC (Model GPC 515A manufactured by Nihon Waters K.K.) equipped with 3 columns of TSKgel SuperHZ2000 (manufactured by

Tosoh Corporation), 1 column of TSKgel SuperHZ4000 (manufactured by Tosoh Corporation) and a refractive index (RI) detector while using tetrahydrofuran as a solvent at a flow rate of 0.6 ml/min and a column temperature of 40°C.

[0068]

2) Softening point

The measurement was made with an automatic softening point measuring apparatus (ASP-M4SP manufactured by Meihosha Factory Ltd.) according to the ring and ball method specified by JIS-K-2207.

[0069]

3) Melt viscosity

The measurement was made with a Brookfield rotational viscometer, CAP2000H, at 150°C.

[0070]

4) Measurement of hydroxyl equivalent

With the use of a potentiometric titration apparatus, the specimen was acetylated with a solution of acetyl chloride (1.5 mol/L) in 1,4-dioxane, the excess of the acetyl chloride was decomposed with water, and the acetic acid formed was titrated with potassium hydroxide (0.5 mol/L).

[0071]

5) Measurement of epoxy equivalent

The specimen was dissolved in methyl ethyl ketone, a solution of tetraethylammonium bromide in acetic acid was added, and the titration was performed with a solution of

perchloric acid (0.1 mol/L) in acetic acid using a potentiometric titration apparatus.

[0072]

6) Gel time

The specimen of epoxy resin composition was placed on a plate, heated to 175°C in advance, of a gel tester (manufactured by Nisshin Kagaku Co., Ltd.), the specimen was stirred with a fluorine polymer stick at a rate of 2 rotations per minute, and the time required for the specimen to harden or the gel time was determined.

[0073]

7) Coefficient of linear expansion (CTE), glass transition point (T_g)

With the use of a thermomechanical measuring apparatus, TMA 120C manufactured by Seiko Instruments Inc., T_g was determined while raising the temperature at a rate of 10°C/min; α_1 (CTE below T_g) was obtained as the mean of the values in the range of 30 to 50°C while α_2 (CTE above T_g) was obtained as the mean of the values in the range of T_g plus 20 to 40°C.

[0074]

8) Bending strength and bending modulus

The measurement was made by the three-point bending test at ambient temperature according to JIS K 6911.

[0075]

9) Adhesive strength

To evaluate the adhesive strength, the tensile shear strength was measured by molding the specimen measuring 25 mm × 12.5 mm × 0.5 mm between 2 copper sheets by a

compression molding machine and post-curing at 180°C for 12 hours.

[0076]

10) Water absorption

The specimen was allowed to absorb water at 85°C and 85% relative humidity, against the standard condition of 25°C and 50% relative humidity, for a period of 100 hours and the change in weight was measured.

[0077]

11) Flame retardancy

The specimen molded with a thickness of 1/16 inch was tested according to UL94 V-0 and the flame retardancy is expressed as the sum of burning time of 5 test specimens.

[0078]

[Table 1]

	Example 3	Comparative Example 1	Comparative Example 2
OCNE	65.1	65.1	99.0
StPN-A	84.9	84.9	51.0
StPN-B			
PN			
Silica	800	800	800
Curing accelerator	1.2	1.2	1.2
Carbon black	5	5	5
Carnauba wax	3	3	3
Content of silica (wt%)	83	83	83

[0079]

[Table 2]

	Example 3	Comparative Example 1	Comparative Example 2
Content of monohydric hydroxy compound (GPC % by area)	1.2	5.5	—
Gel time (s)	27	48	25
Tg (°C)	111	105	165
CTE (<T _g ,×10 ⁻⁵)	1.1	1.2	1.1
CTE (>T _g ,×10 ⁻⁵)	4.8	4.5	4.3
Bending strength (MPa)	110	101	158
Bending modulus (GPa)	19.6	19.0	25.7
Adhesive strength (MPa)	1.33	1.31	1.11
Water absorption (wt%)	0.20	0.20	0.26
Burning time (s)	21	25	332

[0080] Examples 4 and 5 and Comparative Examples 3, 4, and 5

In these examples, StPNE-A obtained in Example 2, StPNE-B obtained in Synthetic Example 2, and an o-cresol novolac type epoxy resin (OCNE: epoxy equivalent 200, softening point 65 °C) were used 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) and a phenol novolac (PN: PSM-4261 manufactured by Gun Ei Chemical Industry Co., Ltd.; OH equivalent 103, softening point 82°C) were used as curing agent components.

Further, spherical silica (average particle diameter 18 μ m) was used as a filler and triphenylphosphine was used as a curing accelerator. They were compounded according to the recipe shown in Table 3 to formulate epoxy resin compositions. The numerical values in the table denote parts by weight.

[0081] These epoxy resin compositions were molded at 175°C and post-cured at 175°C for 12 hours to yield cured products and specimens prepared from the cured products were tested for a variety of properties. The results are shown in Table 4.

[0082]

[Table 3]

	Ex.4	Ex. 5	Comp.Ex.3	Comp.Ex.4	Comp.Ex.5
StPNE-A	99.7	115.7			
StPNE-B			98.0	114.3	
OCNE					80.0
PA	50.3		52.0		70.0
PN		34.3		35.7	
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
Content of silica (wt%)	83	83	83	83	83

[0083]

[Table 4]

	Ex. 4	Ex. 5	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Content of monohydric hydroxy compound (GPC % by area)	1.1	1.1	5.0	5.0	—
Gel time (s)	29	26	45	42	27
T _g (°C)	117	125	110	119	131
CTE (<T _g ,×10 ⁻⁵)	1.1	1.1	1.2	1.2	1.1
CTE (>T _g ,×10 ⁻⁵)	4.8	4.7	4.9	4.7	4.8
Bending strength (MPa)	117	121	115	119	151
Bending modulus (GPa)	20.7	21.3	20.2	20.8	20.2
Adhesive strength (MPa)	1.31	1.26	1.31	1.25	1.14
Water absorption (wt%)	0.22	0.23	0.23	0.24	0.26
Burning time (s)	45	61	59	85	223

Industrial Applicability

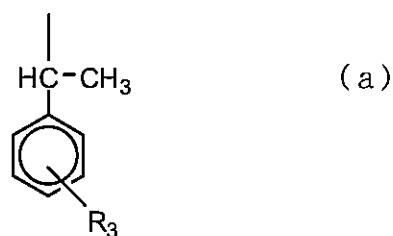
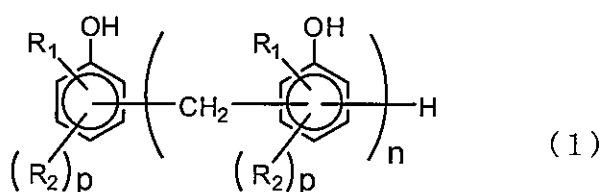
[0084] The epoxy resin and the polyhydric hydroxy resin of this invention, when formulated into an epoxy resin composition, exhibit excellent curing properties and yield a cured product that has excellent flame retardancy, low moisture absorption, and low elasticity and is suitable for applications such as encapsulation of electric and electronic parts and for use as a circuit board material. In particular, they eliminate or reduce the use of flame retardants that

are environmental load substances while exhibiting excellent curing properties and flame retardancy and securing excellent moldability.

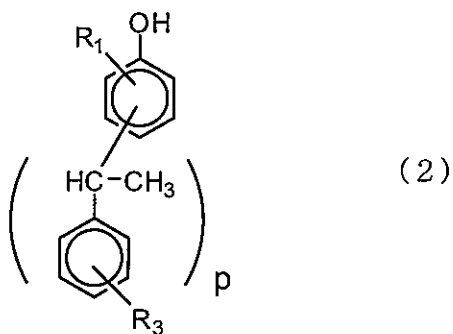
Claims

[Claim 1]

A polyhydric hydroxy resin represented by the following general formula (1) wherein a monohydric hydroxy compound represented by the following general formula (2) accounts for 3% or less by area when detected by gel permeation chromatography (GPC, RI detector);



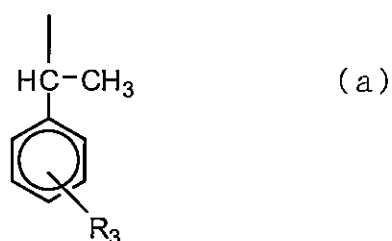
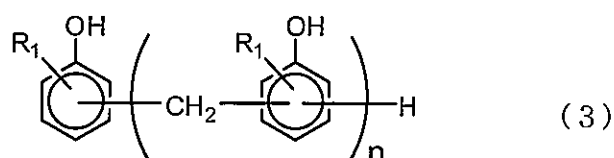
Here, R₁ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms; R₂ is a substituent represented by the following formula (a); n is a number of 0 to 20; p is a number of 0.1 to 2.5; and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms;



Here, p is a number of 0 to 3 and each of R₁ and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms.

[Claim 2]

A method for producing a polyhydric hydroxy resin that comprises reacting a polyhydric hydroxy compound represented by the following general formula (3) with a styrene in the presence of 10 to 400 wt ppm of an acid catalyst at a reaction temperature of 40 to 120°C to introduce a substituent represented by the aforementioned formula (a) to the benzene rings of the polyhydric hydroxy compound;



Here, each of R₁ and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms and n is a number of 1 to 20.

[Claim 3]

A method for producing a polyhydric hydroxy resin described in claim 2 that comprises reacting 1 mole of the hydroxyl group of a polyhydric hydroxy compound represented by general formula (3) with 0.1 to 1.0 mole of a styrene.

[Claim 4]

An epoxy resin composition comprising an epoxy resin and a curing agent wherein a polyhydric hydroxy resin described in claim 1 is an essential component constituting a part or

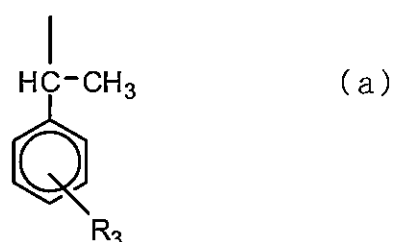
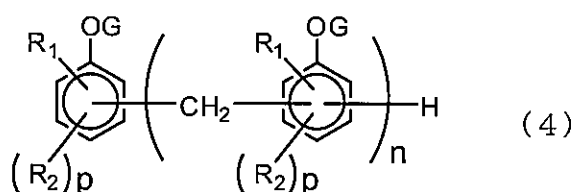
the whole of the curing agent.

[Claim 5]

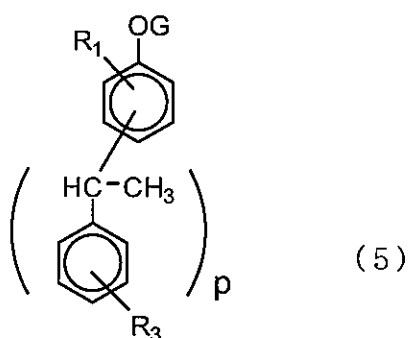
A cured product of epoxy resin produced by curing an epoxy resin composition described in claim 4.

[Claim 6]

An epoxy resin represented by the following general formula (4) wherein a monofunctional epoxy resin represented by the following general formula (5) accounts for 3% or less by area when detected by gel permeation chromatography;



Here, G is a glycidyl group; R₁ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms; R₂ is a substituent represented by formula (a); n is a number of 0 to 20; p is a number of 0.1 to 2.5; and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms;



Here, G is a glycidyl group; p is a number of 0 to 3; and each of R₁ and R₃ is a hydrogen atom or a hydrocarbon group of 1 to 6 carbon atoms.

[Claim 7]

A method for producing an epoxy resin that comprises reacting a polyhydric hydroxy resin described in claim 1 with epichlorohydrin to convert the hydroxyl group of the polyhydric hydroxy resin to a glycidyl ether group.

[Claim 8]

An epoxy resin composition comprising an epoxy resin and a curing agent wherein an epoxy resin described in claim 6 is incorporated as an essential component.

[Claim 9]

A cured product of epoxy resin produced by curing an epoxy resin composition described in claim 8.