

Description

Title of Invention:

EPOXY RESIN, PROCESS FOR PRODUCTION THEREOF, EPOXY RESIN COMPOSITION USING SAME, AND CURED PRODUCT

Technical Field

[0001] The present invention relates to a crystalline epoxy resin, a production method for the resin, an epoxy resin composition using the resin, and a cured product of the composition.

Background Art

[0002] In recent years, development of a base resin having higher performance has been required particularly with advances in fields of advanced materials. For example, in the field of semiconductor sealing, a base resin excellent in high heat resistance and thermal decomposition stability has been required with advances in in-car semiconductors. On the other hand, high-density mounting has been advanced. Hence, a high filling rate of an inorganic filler has been targeted, and the base resin has been strongly required to have a low viscosity. In addition, improvement of high-temperature reliability for corresponding to severe use environments has been required, and improvement of thermal conductivity has been required from the standpoint of improving heat dissipation property.

[0003] However, among conventionally known epoxy resins, one

which satisfies such requirements has not been found yet. For example, Patent Literature 1 proposes a naphthol aralkyl type epoxy resin as an epoxy resin excellent in heat resistance and moisture resistance. However, the resin has insufficient heat resistance and a high viscosity, and hence the resin is not suitable for increasing a filling rate of an inorganic filler. In addition, Patent Literature 2 discloses an aralkyl type epoxy resin obtained by linking 4,4'-dihydroxybiphenyl with a p-xylylene group as an epoxy resin excellent in heat resistance, but the resin has poor moisture resistance and flame resistance. Patent Literature 3 discloses a biphenyl aralkyl type epoxy resin having a structure obtained by linking a bisphenol compound with a biphenylene group, but the resin is a non-crystalline resin-like product. Therefore, the resin has a high viscosity and a high softening point and has poor moldability.

Citation List

Patent Literature

[0004]

[PTL 1] JP 01-252624 A

[PTL 2] JP 04-255714 A

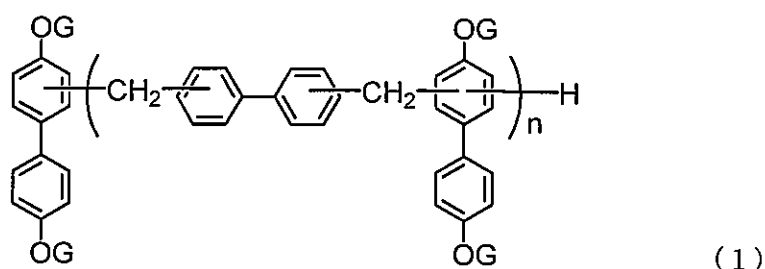
[PTL 3] JP 08-239454 A

Summary of Invention

[0005] Therefore, an object of the present invention is to provide an epoxy resin which is excellent in low viscosity and handling

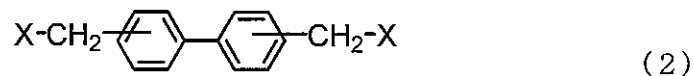
property as a solid, has excellent performance in heat resistance, moisture resistance, and thermal conductivity as well, and is useful for applications such as lamination, molding, casting, and adhesion, an epoxy resin composition using the resin, and a cured product of the composition.

[0006] That is, the present invention relates to an epoxy resin, which is represented by the following general formula (1), exhibits an endothermic peak temperature ranging from 100 to 150°C based on a melting point in differential scanning calorimetry, and is crystalline:

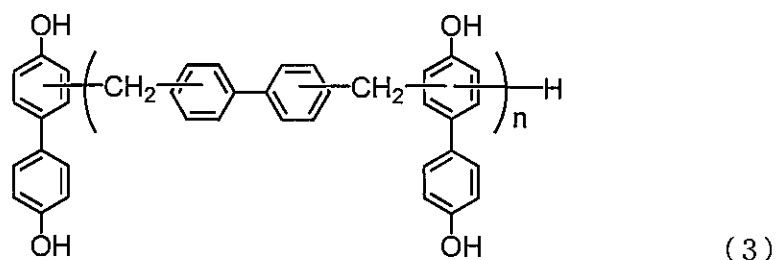


(wherein, n represents 0.2 to 4.0 as an average, and G represents a glycidyl group).

[0007] The present invention also relates to an epoxy resin, which is obtained by subjecting 0.1 to 0.4 mol of a biphenyl-based condensing agent represented by the following general formula (2) to a reaction with 1 mol of 4,4'-dihydroxybiphenyl to prepare a polyhydroxy resin represented by the following general formula (3) and then subjecting the resultant resin to a reaction with epichlorohydrin, exhibits an endothermic peak temperature ranging from 100 to 150°C based on a melting point in differential scanning calorimetry, and is crystalline:



(wherein, **X** represents a hydroxy group, a halogen atom, or an alkoxy group having 1 to 6 carbon atoms); and



(wherein, **n** represents 0.2 to 4.0 as an average).

[0008] The present invention also relates to an epoxy resin composition, including an epoxy resin and a curing agent, in which a component of the epoxy resin includes the above-mentioned epoxy resin, and to a cured product, which is obtained by curing the epoxy resin composition.

Brief Description of Drawings

[0009]

[FIG. 1] A GPC chart of a resin obtained in Reference Example 1.

[FIG. 2] A GPC chart of a resin obtained in Example 1.

[FIG. 3] A DSC chart of a resin obtained in Example 1.

Description of Embodiments

[0010] Hereinafter, the present invention is described in detail.

[0011] An epoxy resin of the present invention is represented by the general formula (1) and is a mixture of components having different numbers of repeating units n . Herein, n represents 0.2 to 4.0 as an average. If the value is smaller than the range, the resin has higher crystallinity and a higher melting point, resulting in deteriorating handling property. If the value is larger than the range, the resin has lower crystallinity and a higher viscosity, resulting in deteriorating moldability. From the standpoints of a low viscosity, handling property, and moldability, the resin preferably has a content of a resin in which n represents 0 within the range of 30 to 60%. In this description, the average of n refers to a number average.

[0012] The epoxy resin of the present invention is crystalline and crystallized in a solid state. The crystalline solid exhibits an endothermic peak temperature of 100 to 150°C, preferably 120 to 150°C, based on a melting point in differential scanning calorimetry measured at a temperature increase rate of 10°C/min. If the temperature is higher than the range, compatibility with a curing agent in preparation of an epoxy resin composition is deteriorated, while if the temperature is lower than the range, a problem such as blocking of the epoxy resin composition occurs, resulting in deteriorating handling property. Although there may be a plurality of melting point peaks depending on the crystal condition of the epoxy resin, the endothermic peak temperature herein refers to one corresponding to the maximum peak. The amount of

endotherm of the peak probably is considered to show a degree of crystallinity, and usually falls within the range of 20 to 80 J/g in terms of resin component. If the amount is smaller than the range, the degree of crystallinity is low, resulting in deteriorating handling property.

[0013] The epoxy resin of the present invention is obtained by subjecting a polyhydroxy resin represented by the general formula (3) to a reaction with epichlorohydrin, but in the invention of the epoxy resin, a production method is not limited thereto. However, the epoxy resin of the present invention can be easily understood by describing the invention of the production method, and hence production methods for the epoxy resin and the polyhydroxy resin to be used as a raw material for the epoxy resin are also described.

[0014] The polyhydroxy resin represented by the general formula (3) is a mixture of components having different values of n , and n represents 0.2 to 4.0 as an average. If the value is smaller than the range, the resin has higher crystallinity, resulting in lowering solubility in epichlorohydrin in synthesis of the epoxy resin, increasing the melting point of the resultant epoxy resin, and deteriorating handling property. If the value is larger than the range, the resin has lower crystallinity and a higher viscosity, resulting in deteriorating moldability. From the standpoints of a low viscosity, handling property, and moldability, the resin preferably has a content of a resin in which $n=0$ within the range of 30 to 60%.

[0015] Such polyhydroxy resin can be obtained by subjecting 4,4'-dihydroxybiphenyl to a reaction with a biphenyl-based condensing agent represented by the general formula (2).

[0016] In the general formula (2), X represents a hydroxy group, a halogen atom, or an alkoxy group having 1 to 6 carbon atoms. Specific examples thereof include 4,4'-bishydroxymethylbiphenyl, 4,4'-bischloromethylbiphenyl, 4,4'-bisbromomethylbiphenyl, 4,4'-bismethoxymethylbiphenyl, and 4,4'-bisethoxymethylbiphenyl. From the standpoint of reactivity, 4,4'-bishydroxymethylbiphenyl and 4,4'-bischloromethylbiphenyl are preferred, and from the standpoint of reducing ionic impurities, 4,4'-bishydroxymethylbiphenyl and 4,4'-bismethoxymethylbiphenyl are preferred.

[0017] In the reaction, the molar ratio of the biphenyl-based condensing agent relative to 1 mol of 4,4'-dihydroxybiphenyl should be 1 mol or less, and falls within the range of generally 0.1 to 0.5 mol, more preferably 0.2 to 0.4 mol. If the ratio is smaller than the range, the resin has high crystallinity, resulting in deteriorating solubility in epichlorohydrin in synthesis of the epoxy resin and the resultant epoxy resin has a higher melting point, resulting in deteriorating handling property. Further, if the ratio is larger than the range, the resin has lower crystallinity and has a higher softening point and melt viscosity, resulting in impairing handling property and moldability.

[0018] In addition, in the case where

4,4'-bischloromethylbiphenyl is used as the condensing agent, the reaction may be carried out in the absence of a catalyst. However, the condensation reaction of the present invention is usually carried out in the presence of an acidic catalyst. The acidic catalyst may be appropriately selected from well-known inorganic acids and organic acids, and examples thereof include: a mineral acid such as hydrochloric acid, sulfuric acid, or phosphoric acid; an organic acid such as formic acid, oxalic acid, trifluoroacetic acid, p-toluenesulfonic acid, methanesulfonic acid, or trifluoromethanesulfonic acid; a Lewis acid such as zinc chloride, aluminum chloride, iron chloride, or boron trifluoride; or a solid acid.

[0019] The reaction is carried out at 10 to 250°C for 1 to 20 hours. In addition, in the reaction, an alcohol such as methanol, ethanol, propanol, butanol, ethylene glycol, methyl cellosolve, or ethyl cellosolve, an aromatic compound such as benzene, toluene, chlorobenzene, or dichlorobenzene, or the like may be used as a solvent. After completion of the reaction, the solvent, or water or an alcohol generated by the condensation reaction is removed, if necessary.

[0020] The polyhydroxy resin thus obtained can be used not only as a raw material for the epoxy resin but also as an epoxy resin curing agent. Moreover, when the resin is used in combination with a curing agent such as hexamine, the resin can be applied as a phenol resin molding material.

[0021] Description is made of the production method for the epoxy resin of the present invention, involving a reaction of the polyhydroxy resin represented by the general formula (3) with epichlorohydrin. The reaction can be carried out in the same manner as a well-known epoxidation reaction.

[0022] Examples of the method include a method involving: dissolving the polyhydroxy resin represented by the general formula (3) in an excessive amount of epichlorohydrin; and then subjecting the mixture to a reaction in the presence of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide at a temperature within the range of 50 to 150°C, preferably at 60 to 120°C for 1 to 10 hours. The amount of epichlorohydrin used in this case falls within the range of 0.8 to 2 mol, preferably 0.9 to 1.2 mol, relative to 1 mol of a hydroxy group in the polyhydroxy resin. 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 solution is filtered and washed with water to remove inorganic salts, and the solvent is distilled off, to thereby obtain an epoxy resin of interest represented by the general formula (1). In the epoxidation reaction, a catalyst such as a quaternary ammonium salt may be used.

[0023] The purity of the epoxy resin of the present invention, in particular, a hydrolyzable chlorine content is preferably small from the standpoint of improving reliability of an electronic part to which the resin is applied. The content is not particularly

limited and is preferably 1,000 ppm or less, more preferably 500 ppm or less. It should be noted that the "hydrolyzable chlorine content" as used in the present invention refers to a value measured by the following method. That is, the value is determined as follows. 0.5 g of a sample is dissolved in 30 ml of dioxane, and 10 ml of 1N-KOH are then added. The mixture is refluxed with boiling for 30 minutes and then cooled to room temperature, and 100 ml of an 80% aqueous solution of acetone are added thereto, followed by potentiometric titration with an aqueous solution of 0.002N-AgNO₃.

[0024] An epoxy resin composition of the present invention includes an epoxy resin and a curing agent, and includes the epoxy resin represented by the general formula (1) as an epoxy resin component.

[0025] The epoxy resin composition of the present invention may include another general epoxy resin having two or more of epoxy groups in the molecule in addition to the epoxy resin represented by the general formula (1) used as an essential component. Examples thereof include: dihydric phenols such as bisphenol A, bisphenol F, 3,3',5,5'-tetramethyl-4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl ketone, fluorenebisphenol, 4,4'-biphenol, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl, 2,2'-biphenol, resorcin, catechol, t-butylcatechol, t-butylhydroquinone, 1,2-dihydroxynaphthalene, 1,3-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 1,5-dihydroxynaphthalene,

1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene,
 1,8-dihydroxynaphthalene, 2,3-dihydroxynaphthalene,
 2,4-dihydroxynaphthalene, 2,5-dihydroxynaphthalene,
 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene,
 2,8-dihydroxynaphthalene, allylated products or polyallylated
 products of the dihydroxynaphthalenes, allylated bisphenol A,
 allylated bisphenol F, and allylated phenol novolac; trihydric or
 more phenols such as phenol novolac, bisphenol A novolac, o-cresol
 novolac, m-cresol novolac, p-cresol novolac, xylenol novolac,
 poly-p-hydroxystyrene, tris-(4-hydroxyphenyl)methane,
 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, fluoroglycinol,
 pyrogallol, t-butylpyrogallol, allylated pyrogallol,
 polyallylated pyrogallol, 1,2,4-benzenetriol,
 2,3,4-trihydroxybenzophenone, a phenol aralkyl resin, a naphthol
 aralkyl resin, and a dicyclopentadiene-based resin; and glycidyl
 etherified compounds derived from halogenated bisphenols 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.

[0026] The epoxy resin composition of the present invention
 includes, as the epoxy resin, the epoxy resin represented by the
 general formula (1) in an amount of desirably 50 wt% or more relative
 to the total amount of the epoxy resin component. The amount is
 more preferably 70 wt% or more, still more preferably 80 wt% or
 more, relative to the total amount of the epoxy resin. If the ratio
 of the resin used is smaller than the values, the resin is deteriorated

in moldability as the epoxy resin composition, and has only small effects of improving heat resistance, moisture resistance, thermal conductivity, solder reflow resistance, and the like when the resin is formed into a cured product.

[0027] As the curing agent in the epoxy resin composition of the present invention, all generally known curing agents for epoxy resins can be used. Examples thereof include dicyandiamide, polyphenols, acid anhydrides, and aromatic and aliphatic amines. In the field of sealing of electric and electronic parts, which requires moisture resistance and heat resistance, the polyphenols are preferably used. Specific examples of the polyphenols are shown below. In the resin composition of the present invention, one kind of those curing agents may be used or two or more kinds thereof may be used as a mixture.

[0028] Examples of the polyphenols include: dihydric phenols such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, and naphthalenediol; trihydric or more phenols represented by tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, phenol novolac, o-cresol novolac, naphthol novolac, polyvinylphenol, and the like; and phenols, naphthols, or polyphenolic compounds synthesized with dihydric phenols such as bisphenol A, bisphenol F, bisphenol S, fluorenebisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, resorcin, and naphthalenediol and condensing agents such as

formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, and p-xylylene glycol. In addition, a polyhydroxy resin represented by the general formula (3) may also be used.

[0029] Examples of the acid anhydrides include phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, methyl Himic anhydride, nadic anhydride, and trimellitic anhydride.

[0030] 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.

[0031] For the resin composition of the present invention, one kind of those curing agents may be used or two or more kinds thereof may be used as a mixture.

[0032] In addition, in the epoxy resin composition of the present invention, an oligomer or polymer such as polyester, polyamide, polyimide, polyether, polyphenylene ether, polyurethane, a petroleum resin, an indene-coumarone resin, or a phenoxy resin may be appropriately blended, and various additives such as an organic filler, a pigment, a flame retardant, a thixotropy-imparting agent, a coupling agent, and a flow improver may be blended.

[0033] In addition, in the epoxy resin composition of the

present invention, an inorganic filler can be blended. For example, spherical or granular molten silica, silica powder such as crystal silica, powder or spheroidized beads of alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, boron nitride, beryllia, zirconia, forsterite, steatite, spinel, mullite, titania, or the like, single crystal fiber of potassium titanate, silicon carbide, silicon nitride, alumina, or the like, and glass fiber may be used alone or in combination of two or more kinds thereof. Of the above-mentioned inorganic fillers, molten silica is preferred from the standpoint of reducing a linear expansion coefficient, and alumina is preferred from the standpoint of high thermal conductivity. As the form of the filler, it is preferred that 50% or more of the filler be spherical from the standpoints of flowability and mold abrasion resistance when the resin composition is molded, and spherical molten silica powder is particularly preferably used.

[0034] The amount of the inorganic filler added is usually 50 wt% or more, preferably 70 wt% or more, more preferably 80 wt% or more, relative to the amount of the epoxy resin composition. If the amount is smaller than the value, effects of interest in the present invention, such as low moisture absorbability, low thermal expandability, high heat resistance, and high thermal conductivity, cannot be exerted sufficiently. The effects are more improved when the amount of the inorganic filler added is larger. However, the effects are not improved in parallel with the volume fraction of the inorganic filler and are improved drastically with a specific

amount or more of the inorganic filler. On the other hand, if the amount of the inorganic filler added is larger than the amount, the viscosity is increased, resulting in deteriorating moldability, which is not preferred.

[0035] In the epoxy resin composition of the present invention, a known curing promoter may be blended. Examples thereof include amines, imidazoles, organic phosphines, and Lewis acids. Specific examples thereof include cycloamidine compounds such as 1,8-diazabicyclo(5,4,0)undecene-7, 1,5-diaza-bicyclo(4,3,0)nonene, and 5,6-dibutylamino-1,8-diaza-bicyclo(5,4,0)undecene-7, and compounds having intramolecular polarization obtained by addition of the cycloamidine compounds with compounds having π bonds such as maleic anhydride, benzoquinone, and diazophenylmethane, tertiary amines such as triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, and tris(dimethylaminomethyl)phenol and derivatives thereof, imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, and 2-heptadecylimidazole and derivatives thereof, organic phosphines such as tributylphosphine, methyldiphenylphosphine, triphenylphosphine, diphenylphosphine, and phenylphosphine, and phosphorus compounds having intramolecular polarization obtained by addition of the phosphines with compounds having π bonds such as maleic anhydride, benzoquinone, and diazophenylmethane, tetra-substituted phosphonium

tetra-substituted borates such as tetraphenylphosphonium tetraphenylborate, tetraphenylphosphonium ethyltriphenylborate, and tetrabutylphosphonium tetrabutylborate, tetraphenyl boron salts such as 2-ethyl-4-methylimidazole tetraphenylborate and N-methylmorpholine tetraphenylborate, and derivatives thereof. The amount of the curing promoter added usually falls within the range of 0.2 to 10 parts by weight relative to 100 parts by weight of the epoxy resin. These may be used alone or in combination.

[0036] For the epoxy resin composition of the present invention, a flame retardant is used as needed. Examples of the flame retardant include phosphorus-based flame retardants such as red phosphorus and phosphate compounds, nitrogen-based flame retardants such as triazine derivatives, phosphorus-nitrogen-based flame retardants such as phosphazene derivatives, metal oxides, metal hydrates, organometal complexes such as metallocene derivatives, and zinc compounds such as zinc borate, zinc stannate, and zinc molybdate. Of those, metal hydrates are preferred. Examples of the metal hydrates include aluminum hydroxide, magnesium hydroxide, calcium hydroxide, nickel hydroxide, cobalt hydroxide, iron hydroxide, tin hydroxide, zinc hydroxide, copper hydroxide, and titanium hydroxide. Further, complex metal hydrates of these metal hydrates with metal oxides such as nickel oxide, cobalt oxide, iron oxide, tin oxide, zinc oxide, copper oxide, and palladium oxide may be used. Magnesium hydroxide is preferred in view of influences on safety, a flame retardant effect, and moldability of a molding material.

[0037] In the epoxy resin composition of the present invention, other than the above-mentioned compounds, parting agents such as higher fatty acids, metal salts of higher fatty acids, ester-based wax, and polyolefin wax, coloring agents such as carbon black, coupling agents such as silane-based, titanate-based, and aluminate-based coupling agents, flexibilizers such as silicone powder, stress relaxation agents such as silicone oil or silicone rubber powder, ion-trapping agents such as hydrotalcite and antimony-bismuth, and the like may be used as needed.

[0038] In addition, in the epoxy resin composition of the present invention, from the standpoints of improving flowability when the resin composition is molded and improving adhesion with a substrate such as a lead frame, a thermoplastic oligomer may be added. Examples of the thermoplastic oligomer include C5 and C9 petroleum resins, a styrene resin, an indene resin, an indene-styrene copolymer resin, an indene-styrene-phenol copolymer resin, an indene-coumarone copolymer resin, and an indene-benzothiophene copolymer resin. The amount of the thermoplastic oligomer added typically falls within the range of 2 to 30 parts by weight relative to 100 parts by weight of the epoxy resin.

[0039] As a preparation method for the epoxy resin composition of the present invention, any technology may be used as long as various raw materials may be dispersed and mixed homogeneously. As a general method, there is given a method involving: mixing predetermined blending amounts of raw materials sufficiently using

a mixer or the like; melting and kneading the mixture using a mixing roll, an extruder, or the like; and cooling and pulverizing the resultant product.

[0040] The epoxy resin composition of the present invention is particularly suitable for sealing of a semiconductor device.

[0041] A cured product of the present invention can be obtained by thermally curing the epoxy resin composition. In order to obtain the cured product using the epoxy resin composition of the present invention, a method such as transfer molding, press molding, cast molding, injection molding, or extrusion molding may be employed, and from the standpoint of high-volume production, transfer molding is preferred.

Examples

[0042] Hereinafter, the present invention is described more specifically by way of examples.

[0043] Synthesis Example 1

186.0 g (1.0 mol) of 4,4'-dihydroxybiphenyl and 600 g of diethylene glycol dimethyl ether were charged to a 2,000-ml four-necked flask, and the mixture was heated with stirring to 150°C under a nitrogen stream. A solution obtained by dissolving 75.3 g (0.3 mol) of 4,4'-bischloromethylbiphenyl in 260 g of diethylene glycol dimethyl ether was added dropwise, and the mixture was then heated to 170°C and subjected to a reaction for 2 hours. After the reaction, the mixture was added dropwise to a large volume of pure

water to collect the product by reprecipitation, to thereby obtain 220 g of a pale-yellow crystalline resin. The resultant resin was found to have an OH equivalent of 130.8. The peak temperature in DSC measurement was 248.5°C, and the amount of endotherm caused by melting of a crystal was 95.5 J/g. FIG. 1 shows a GPC chart of the resultant resin. The ratios of components each represented by the general formula (3), determined by GPC measurement, were as follows: $n=0$; 39.33%, $n=1$; 22.25%, $n=2$; 12.19%, $n=3$; 8.14%, $n=4$; 5.58%, and $n\geq 5$; 11.88%. Herein, the DSC peak temperature refers to a value measured using a differential scanning calorimeter (manufactured by Seiko Instruments Inc., type DSC 220C) at a temperature increase rate of 5°C/min. In addition, GPC measurement was carried out under the following conditions: device; manufactured by Nihon Waters K.K., type 515A, column; TSK-GEL 2000×3 and TSK-GEL 4000×1 (both of which are manufactured by TOSOH CORPORATION), solvent; tetrahydrofuran, flow rate; 1 ml/min, temperature; 38°C, detector; RI.

[0044] Synthesis Example 2

A reaction was carried out in the same manner as in Example 1, except that 167.4 g (0.9 mol) of 4,4'-dihydroxybiphenyl, 540 g of diethylene glycol dimethyl ether, and a solution obtained by dissolving 90.4 g (0.36 mol) of 4,4'-bischloromethylbiphenyl in 320 g of diethylene glycol dimethyl ether were used. Thus, 205 g of a pale-yellow crystalline resin were obtained. The resultant resin was found to have an OH equivalent of 139.2. The DSC peak

temperature was 242.4°C, and the ratios of components each represented by the general formula (3), determined by GPC measurement, were as follows: $n=0$; 31.21%, $n=1$; 21.19%, $n=2$; 13.38%, $n=3$; 10.63%, $n=4$; 7.55%, and $n\geq 5$; 15.35%.

[0045] Synthesis Example 3

A reaction was carried out in the same manner as in Example 1, except that 186.0 g (1.0 mol) of 4,4'-dihydroxybiphenyl, 540 g of diethylene glycol dimethyl ether, and a solution obtained by dissolving 50.2 g (0.2 mol) of 4,4'-bischloromethylbiphenyl in 320 g of diethylene glycol dimethyl ether were used. Thus, 195 g of a pale-yellow crystalline resin were obtained. The resultant resin was found to have an OH equivalent of 125.6. The DSC peak temperature was 255.4°C, and the ratios of components each represented by the general formula (3), determined by GPC measurement, were as follows: $n=0$; 50.87%, $n=1$; 20.67%, $n=2$; 11.54%, $n=3$; 7.11%, $n=4$; 3.78%, and $n\geq 5$; 5.87%.

[0046] Synthesis Example 4

A reaction was carried out in the same manner as in Example 1, except that 152.5 g (0.82 mol) of 4,4'-dihydroxybiphenyl, 500 g of diethylene glycol dimethyl ether, and a solution obtained by dissolving 112.9 g (0.45 mol) of 4,4'-bischloromethylbiphenyl in 360 g of diethylene glycol dimethyl ether were used. Thus, 201 g of a pale-yellow resin were obtained. The resultant resin was found to have an OH equivalent of 150.1. The ratios of components each represented by the general formula (3), determined by GPC measurement,

were as follows: $n=0$; 22.03%, $n=1$; 14.65%, $n=2$; 11.89%, $n=3$; 9.46%, $n=4$; 7.36%, and $n\geq 5$; 33.87%.

[0047] Synthesis Example 5

A reaction was carried out in the same manner as in Example 1, except that 186.0 g (1.0 mol) of 4,4'-dihydroxybiphenyl, 600 g of diethylene glycol dimethyl ether, and a solution obtained by dissolving 52.5 g (0.3 mol) of 1,4-bis(chloromethyl)benzene in 260 g of diethylene glycol dimethyl ether were used. Thus, 202 g of a pale-yellow crystalline resin were obtained. The resultant resin was found to have an OH equivalent of 116.3. The DSC peak temperature was 241.7°C, and the ratios of components corresponding to structures each represented by the general formula (3) in which the biphenylene group serving as a crosslinking site was replaced by a phenylene group, determined by GPC measurement, were as follows: $n=0$; 40.33%, $n=1$; 23.31%, $n=2$; 11.22%, $n=3$; 7.09%, $n=4$; 5.17%, and $n\geq 5$; 12.35%.

[0048] Synthesis Example 6

A reaction was carried out in the same manner as in Synthesis Example 1, except that 200.0 g (1.0 mol) of 4,4'-dihydroxydiphenylmethane were used instead of 4,4'-dihydroxybiphenyl (1.0 mol), and then the solvent was distilled off under reduced pressure. Thus, 245 g of a pale-brown resin were obtained. The resultant resin was found to have an OH equivalent of 137.6. The ratios of components corresponding to structures each represented by the general formula (3) in which the 4,4'-dihydroxybiphenyl skeleton was replaced by

4,4'-dihydroxydiphenylmethane, determined by GPC measurement, were as follows: $n=0$; 36.89%, $n=1$; 20.36%, $n=2$; 12.30%, $n=3$; 9.68%, $n=4$; 6.58%, and $n\geq 5$; 13.56%.

[0049] Example 1

120 g of the resin obtained in Synthesis Example 1 were dissolved in 509 g of epichlorohydrin and 76.4 g of diethylene glycol dimethyl ether, and 76.5 g of a 48% aqueous solution of sodium hydroxide were added dropwise under reduced pressure (about 130 Torr) at 62°C over 4 hours. During the procedure, the generated water was removed from the system by azeotropy with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After completion of the dropwise addition, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, and 971 g of methyl isobutyl ketone were added thereto, followed by washing with water to remove salts. Thereafter, 19.3 g of a 24% aqueous solution of sodium hydroxide were added thereto, and the mixture was subjected to a reaction at 85°C for 2 hours. After completion of the reaction, the mixture was filtered and washed with water, and methyl isobutyl ketone used as a solvent was then distilled off under reduced pressure, to thereby obtain 148 g of an epoxy resin (epoxy resin A). The resin was found to have an epoxy equivalent of 183.7 and a hydrolyzable chlorine content of 1,400 ppm. FIG. 2 shows a GPC chart of the resultant resin. The ratios of components each represented by the general formula (1), determined by GPC measurement, were as follows: $n=0$; 42.49%, $n=1$; 19.41%, $n=2$; 12.23%, $n=3$; 8.50%, $n=4$; 4.56%, and

$n \geq 5$; 8.18%. FIG. 3 shows the results of DSC measurement. In the results of DSC measurement, the peak temperature was 140.0°C, and the amount of endotherm caused by melting of a crystal was 36.9 J/g. In addition, the capillary melting point was 111.5 to 143.8°C, and the melt viscosity at 150°C was 51 mPa·s.

[0050] Example 2

122 g of the resin obtained in Synthesis Example 2 were dissolved in 486 g of epichlorohydrin and 72.9 g of diethylene glycol dimethyl ether, and 73.0 g of a 48% aqueous solution of sodium hydroxide were added dropwise under reduced pressure (about 130 Torr) at 62°C over 4 hours. During the procedure, the generated water was removed from the system by azeotropy with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After completion of the dropwise addition, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, and 970 g of methyl isobutyl ketone were added thereto, followed by washing with water to remove salts. Thereafter, 19.3 g of a 24% aqueous solution of sodium hydroxide were added thereto, and the mixture was subjected to a reaction at 85°C for 2 hours. After completion of the reaction, the mixture was filtered and washed with water, and methyl isobutyl ketone used as a solvent was then distilled off under reduced pressure, to thereby obtain 146 g of an epoxy resin (epoxy resin B). The resin was found to have an epoxy equivalent of 195.1 and a hydrolyzable chlorine content of 715 ppm. In DSC measurement, the peak temperature was 135.1°C, and the amount of endotherm caused by melting of a

crystal was 29.8 J/g. In addition, the capillary melting point was 107.8 to 140.1°C, and the melt viscosity at 150°C was 95 mPa·s. The ratios of components each represented by the general formula (1), determined by GPC measurement, were as follows: $n=0$; 32.25%, $n=1$; 18.42%, $n=2$; 12.85%, $n=3$; 9.42%, $n=4$; 6.01%, and $n\geq 5$; 16.63%.

[0051] Example 3

110 g of the resin obtained in Synthesis Example 3 were dissolved in 486 g of epichlorohydrin and 71.5 g of diethylene glycol dimethyl ether, and 70.8 g of a 48% aqueous solution of sodium hydroxide were added dropwise under reduced pressure (about 130 Torr) at 62°C over 4 hours. During the procedure, the generated water was removed from the system by azeotropy with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After completion of the dropwise addition, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, and 972 g of methyl isobutyl ketone were added thereto, followed by washing with water to remove salts. Thereafter, 15.5 g of a 24% aqueous solution of sodium hydroxide were added thereto, and the mixture was subjected to a reaction at 85°C for 2 hours. After completion of the reaction, the mixture was filtered and washed with water, and methyl isobutyl ketone used as a solvent was then distilled off under reduced pressure, to thereby obtain 149 g of an epoxy resin (epoxy resin C). The resin was found to have an epoxy equivalent of 182.4 and a hydrolyzable chlorine content of 675 ppm. In DSC measurement, the peak temperature was 146.1°C, and the amount of endotherm caused by melting of a

crystal was 46.1 J/g. In addition, the capillary melting point was 118.2 to 147.0°C, and the melt viscosity at 150°C was 36 mPa·s. The ratios of components each represented by the general formula (1), determined by GPC measurement, were as follows: $n=0$; 49.16%, $n=1$; 20.11%, $n=2$; 10.52%, $n=3$; 6.51%, $n=4$; 3.98%, and $n\geq 5$; 6.65%.

[0052] Comparative Example 1

125 g of the resin obtained in Synthesis Example 4 were dissolved in 462 g of epichlorohydrin and 69.3 g of diethylene glycol dimethyl ether, and 69.4 g of a 48% aqueous solution of sodium hydroxide were added dropwise under reduced pressure (about 130 Torr) at 62°C over 4 hours. During the procedure, the generated water was removed from the system by azeotropy with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After completion of the dropwise addition, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, and 972 g of methyl isobutyl ketone were added thereto, followed by washing with water to remove salts. Thereafter, 19.3 g of a 24% aqueous solution of sodium hydroxide were added thereto, and the mixture was subjected to a reaction at 85°C for 2 hours. After completion of the reaction, the mixture was filtered and washed with water, and methyl isobutyl ketone used as a solvent was then distilled off under reduced pressure, to thereby obtain 148 g of an epoxy resin (epoxy resin D). The resin was found to have an epoxy equivalent of 209.2 and a hydrolyzable chlorine content of 621 ppm. In addition, as the crystallinity of the resultant resin was low, no clear melting point was observed

in DSC. The melt viscosity at 150°C was 0.52 Pa·s. The ratios of components each represented by the general formula (1), determined by GPC measurement, were as follows: $n=0$; 20.75%, $n=1$; 12.48%, $n=2$; 10.59%, $n=3$; 8.57%, $n=4$; 5.99%, and $n\geq 5$; 37.11%.

[0053] Comparative Example 2

115 g of the resin obtained in Synthesis Example 5 were dissolved in 549 g of epichlorohydrin and 82.4 g of diethylene glycol dimethyl ether, and 82.4 g of a 48% aqueous solution of sodium hydroxide were added dropwise under reduced pressure (about 130 Torr) at 62°C over 4 hours. During the procedure, the generated water was removed from the system by azeotropy with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After completion of the dropwise addition, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, and 966 g of methyl isobutyl ketone were added thereto, followed by washing with water to remove salts. Thereafter, 19.2 g of a 24% aqueous solution of sodium hydroxide were added thereto, and the mixture was subjected to a reaction at 85°C for 2 hours. After completion of the reaction, the mixture was filtered and washed with water, and methyl isobutyl ketone used as a solvent was then distilled off under reduced pressure, to thereby obtain 145 g of an epoxy resin (epoxy resin E). The resin was found to have an epoxy equivalent of 173.0 and a hydrolyzable chlorine content of 490 ppm. In DSC measurement, the peak temperature was 133.6°C, and the amount of endotherm caused by melting of a crystal was 47.6 J/g. In addition, the capillary melting point was

110.0 to 142.0°C, and the melt viscosity at 150°C was 42 mPa·s. The ratios of components each represented by the general formula (1), determined by GPC measurement, were as follows: $n=0$; 42.92%, $n=1$; 19.64%, $n=2$; 11.46%, $n=3$; 7.67%, $n=4$; 4.91%, and $n\geq 5$; 10.64%.

[0054] Comparative Example 3

120 g of the resin obtained in Synthesis Example 6 were dissolved in 484 g of epichlorohydrin and 62.9 g of diethylene glycol dimethyl ether, and 69.0 g of a 48% aqueous solution of sodium hydroxide were added dropwise under reduced pressure (about 130 Torr) at 62°C over 4 hours. During the procedure, the generated water was removed from the system by azeotropy with epichlorohydrin, and the distilled epichlorohydrin was returned to the system. After completion of the dropwise addition, the reaction was continued for another hour. After that, epichlorohydrin was distilled off, and 956 g of methyl isobutyl ketone were added thereto, followed by washing with water to remove salts. Thereafter, 17.6 g of a 24% aqueous solution of sodium hydroxide were added thereto, and the mixture was subjected to a reaction at 85°C for 2 hours. After completion of the reaction, the mixture was filtered and washed with water, and methyl isobutyl ketone used as a solvent was then distilled off under reduced pressure, to thereby obtain 152.5 g of a pale-brown noncrystalline epoxy resin (epoxy resin F). The resin was found to have an epoxy equivalent of 193.5 and a hydrolyzable chlorine content of 450 ppm. The resin was found to have a softening point of 82°C and a melt viscosity at 150°C of 68 mPa·s. The ratios of components having structures

each represented by the general formula (1) in which the 4,4'-dihydroxybiphenyl skeleton was replaced by 4,4'-dihydroxydiphenylmethane, determined by GPC measurement, were as follows: $n=0$; 34.54%, $n=1$; 18.65%, $n=2$; 12.34%, $n=3$; 10.69%, $n=4$; 8.20%, and $n\geq 5$; 15.22%.

[0055] Examples 4 to 6 and Comparative Examples 4 to 7

The epoxy resins obtained in Examples 1 to 3 (epoxy resins A to C) and the epoxy resins obtained in Comparative Examples 1 to 3 (epoxy resins D to F) were used as epoxy resin components, and phenol novolac (manufactured by Gunee Chemical Industry Co., Ltd., PSM-4261; OH equivalent: 103, softening point: 82°C) was used as a curing agent. In addition, triphenylphosphine was used as a curing promoter, and spherical alumina (mean particle size: 12.2 μm) was used as an inorganic filler. The components shown in Table 1 were blended, mixed well using a mixer, and kneaded using a heating roll for about 5 minutes, and the resultant products were cooled and pulverized, to thereby obtain epoxy resin compositions of Examples 4 to 6 and Comparative Examples 4 to 7. The epoxy resin compositions were molded at 175°C for 5 minutes and postcured at 180°C for 12 hours, to thereby obtain cured molded products, and physical properties of the products were evaluated.

[0056] The results are collectively shown in Table 1. It should be noted that the numerals for the respective components in Table 1 refer to parts by weight. In addition, evaluation was carried out as follows. Further, the molded product of Comparative Example

4 had very poor flowability and was difficult to mold, and hence physical properties of the molded product were not be able to be evaluated.

[0057] (1) Thermal conductivity: measured by a transient hot wire method using a thermal conductivity meter manufactured by NETZSCH, type LFA 447.

(2) Thermal expansion coefficient and glass transition temperature: measured at a temperature increase rate of 10°C/min using a thermomechanical measuring device manufactured by Seiko Instruments Inc., type TMA 120C.

(3) Water absorption rate: a disc having a diameter of 50 mm and a thickness of 3 mm was molded, postcured, and allowed to absorb moisture at 85°C at a relative humidity of 85% for 100 hours, and the rate of change in weight was determined.

(4) Gelation time: an epoxy resin composition was poured into the concave portion in a gelation tester (manufactured by Nisshin Chemical Co., Ltd.) preliminarily heated to 175°C and stirred at a rate of two revolutions per second using a PTFE stirring bar, and a gelation time required for curing the epoxy resin composition was determined.

(5) Spiral flow: an epoxy resin composition was molded using a mold for spiral flow measurement based on a standard (EMMI-1-66) under the conditions of a spiral flow injection pressure (150 kgf/cm²), a curing temperature of 175°C, and a curing time of 3 minutes, and a flow length was then examined.

[0058]

[Table 1]

	Example			Comparative Example			
	1	2	3	4	5	6	7
Epoxy resin A	96.0						
Epoxy resin B		98.0					
Epoxy resin C			96.0				
Epoxy resin D				100.5	100.5		
Epoxy resin E						94.0	
Epoxy resin F							98.0
Curing agent	54.0	52.0	54.0	49.5	49.5	56.0	52.0
Inorganic filler	1350	1350	1350	1350	800	1350	1350
Curing promoter	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Gelation time (s)	33	32	31	27	28	31	34
Spiral flow (cm)	102	94	86	15	45	89	105
Glass transition temperature (°C)	194	203	187		204	178	147
Thermal expansion coefficient (ppm, <T _g)	10.0	10.0	10.4		15.4	10.6	11.1
Thermal expansion coefficient (ppm, >T _g)	47.0	46.6	51.2		73.1	55.3	57.4
Water absorption rate (wt%, 100h)	0.19	0.17	0.19		0.24	0.23	0.22
Thermal conductivity (W/m·K)	4.50	4.84	4.47		3.52	3.60	3.53

Industrial Applicability

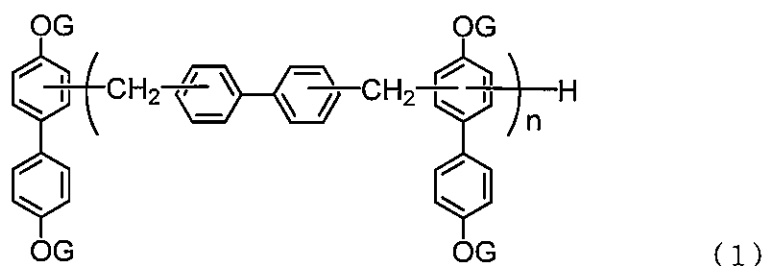
[0059] The epoxy resin of the present invention is excellent in handling property as a solid because the resin is crystalline and has a melting point, and is excellent in moldability as well because the resin has a low viscosity. In addition, in the case where the resin is applied to an epoxy resin composition, a cured product excellent in high heat resistance, thermal decomposition

stability, and high thermal conductivity can be produced and suitably used for applications such as sealing of electric and electronic parts and a circuit board material. Moreover, the epoxy resin produced according to the present invention can provide a cured product which is excellent in low viscosity and handling property as a solid and is excellent in heat resistance, moisture resistance, and thermal conductivity as well, and the product is suitably used as an insulating material or the like used in the electric and electronic field, such as a printed circuit board, a heat dissipation substrate, or a semiconductor sealing.

Claims

[Claim 1]

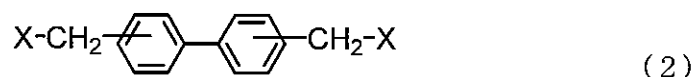
An epoxy resin, which is represented by the following general formula (1), exhibits an endothermic peak temperature ranging from 100 to 150°C based on a melting point in differential scanning calorimetry, and is crystalline:



where **n** represents 0.2 to 4.0 as an average, and **G** represents a glycidyl group.

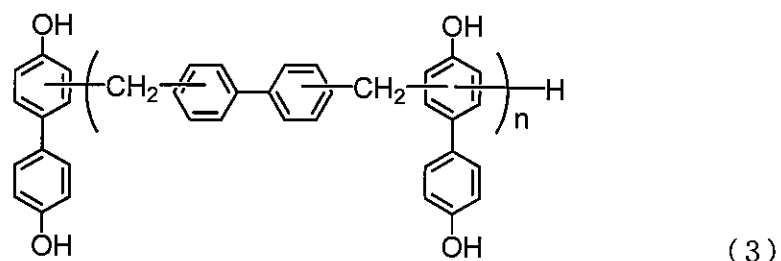
[Claim 2]

An epoxy resin, which is obtained by subjecting 0.1 to 0.4 mol of a biphenyl-based condensing agent represented by the following general formula (2) to a reaction with 1 mol of 4,4'-dihydroxybiphenyl to prepare a polyhydroxy resin represented by the following general formula (3) and then subjecting the resultant resin to a reaction with epichlorohydrin, exhibits an endothermic peak temperature ranging from 100 to 150°C based on a melting point in differential scanning calorimetry, and is crystalline:



where **X** represents a hydroxy group, a halogen atom, or an alkoxy

group having 1 to 6 carbon atoms; and



where **n** represents 0.2 to 4.0 as an average.

[Claim 3]

An epoxy resin according to claim 1, wherein a content of the epoxy resin represented by the general formula (1) where **n** represents 0 ranges from 30 to 60%.

[Claim 4]

An epoxy resin according to claim 1, which has a softening point of 100 to 150°C and a melt viscosity at 150°C of 0.02 to 0.2 Pa·s.

[Claim 5]

An epoxy resin composition, comprising an epoxy resin and a curing agent, wherein a component of the epoxy resin comprises the epoxy resin according to any one of claims 1 to 4.

[Claim 6]

A cured product, which is obtained by curing the epoxy resin composition according to claim 5.