

TITLE OF THE INVENTION

Epoxy Resin and Epoxy Resin Composition

BACKGROUND OF THE INVENTION

This invention relates to an epoxy resin and an epoxy resin composition comprising said epoxy resin. In particular, this invention is directed to an epoxy resin which exhibits low viscosity upon mixing with a curing agent to enable a convenient shaping, and which, once cured, has an excellent heat resistance and a high mechanical strength. This invention is also directed to an epoxy resin composition which exhibits excellent impregnation into such materials as a glass cloth, and which, once cured, exhibits high heat resistance and blister resistance to enable its use in the production of a copper clad epoxy resin laminate for a printed wiring board, in particular, a multilayered printed wiring board.

Plastic composite materials prepared by blending a matrix of a plastic material and a reinforcement are widely used in industry since they have excellent heat resistance, weatherability, chemical resistance, or mechanical strength. Epoxy resins are widely employed for the matrix of the plastic composite material since they have favorable dynamic properties, and they are highly adhesive to the reinforcing fibers used for the reinforcement, and the resulting composite materials are readily shapable.

Among such plastic composite materials, the one comprising an epoxy resin and a carbon fiber is highly expected to be the most significant next generation structural material in aerospace, automobile, and other high technology industries in view of its excellent heat resistance and mechanical strength.

However, the composite materials are expected to have an even higher heat resistance and a further improved shapability or moldability to enable their use as structural materials in such high technology fields.

Recently, range of electronic appliances have greatly increased, and multilayer printed wiring boards are finding their use not only in computer-related equipments but also in automatically controlled machines, communication equipments, business machines, game machines, and the like for their improvement in performance and size reduction.

On the other hand, in the field of computers, system construction have undergone a significant change as often referred to as downsizing, and a distributed system constructed around a work station have become common. The printed wiring boards used in such distributed system were not developed in the direction of increasing the number of layers in the laminate, and they usually comprise a laminate of four to ten layers. In the printed wiring boards of such field, fine patterns to realize high density packaging as well as thickness reduction are under investigation.

To correspond to such requirements imposed on printed wiring boards, the substrates used for the wiring boards should have even more improved heat resistance and blister resistance.

One method known in the art for improving the heat resistance of the epoxy resin is addition of a polyfunctional epoxy resin to thereby increase crosslinking density of the resin. Novolak epoxy resin is widely used in such modification because of its inexpensive price.

Novolak epoxy resin, however, has a considerably wide molecular weight distribution, and when the novolak epoxy resin is added in a large amount, or when the novolak epoxy resin of a high molecular weight is used, the resulting resin would have an excessively high viscosity. When such resin of high viscosity is used for the matrix of the plastic composite material, it would become difficult to fully impregnate the reinforcing fiber with the matrix resin and to shape the resulting plastic composite material. Also, severe requirements in heat resistance imposed on laminates for printed wiring boards were not fulfilled by mere addition of the polyfunctional epoxy resin. For example, an improvement in heat resistance by an excessive addition of such a polyfunctional epoxy resin would result in hardening of the composition to brittleness, and when the laminate produced from such a composition is subjected to soldering after boiling, there often occurred ply separation to result in blisters.

SUMMARY OF THE INVENTION

First object of the present invention is to provide a readily shapable epoxy resin which, upon mixing with a curing agent, exhibits a low viscosity, and which, once cured, exhibits an excellent heat resistance as well as a high mechanical strength.

Second object of the present invention is to provide an epoxy resin composition which exhibits an excellent impregnation into materials such as glass cloth, and which, once cured, exhibits excellent heat resistance, blister resistance, and adhesion to copper clad, and consequently, which is well suited for use in the production of a copper clad epoxy resin laminate for a printed wiring board, in particular, a multilayer printed wiring board.

The inventors of the present invention have made an intensive study to attain the above-mentioned first object, and found out that a readily shapable epoxy resin of low viscosity which, once cured, exhibits an excellent heat resistance as well as a high mechanical strength may be produced by effecting the glycidyl etherification of a bisphenol with an epihalohydrin or a methylepihalohydrin in the presence of a novolak resin to thereby simultaneously effect the glycidyl etherification of the bisphenol and the novolak resin.

To attain the above-mentioned first object of the invention, there is provided in accordance with the present invention, an epoxy resin (A) produced by glycidyl

etherifying a bisphenol (I) and a novolak resin (II) with at least one member selected from an epihalohydrin and a methylepihalohydrin.

Furthermore, to attain the above-mentioned second object of the invention, there is provided in accordance with the present invention an epoxy resin composition mainly comprising a polyadduct epoxy resin (B) produced by glycidyl etherifying a bisphenol (I) and a novolak resin (II) with at least one member selected from an epihalohydrin and a methylepihalohydrin to produce an epoxy resin (A), and then reacting the epoxy resin (A) with a halogenated bisphenol (III) in the presence of an onium salt or a base catalyst to produce the polyadduct resin (B).

Still further, to attain the above-mentioned second object of the invention, there is also provided in accordance with the present invention an epoxy resin composition mainly comprising a polyadduct epoxy resin (D) produced by glycidyl etherifying a bisphenol (I), a novolak resin (II), and a halogenated bisphenol (III) with an epihalohydrin or a methylepihalohydrin to produce an epoxy resin (C), and then reacting the epoxy resin (A) with a halogenated bisphenol (III) in the presence of an onium salt or a base catalyst to produce the polyadduct resin (D).

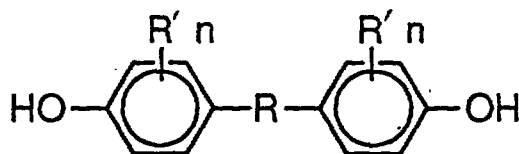
DETAILED DESCRIPTION OF THE INVENTION

The epoxy resin of the present invention and the epoxy resin composition containing such epoxy resin are hereinafter described in detail.

The epoxy resin (A) of the present invention is produced by using a bisphenol (I) and a novolak resin (II) as its starting materials. The epoxy resin composition of the present invention mainly comprises a polyadduct epoxy resin (B) or (D) respectively produced by reacting the epoxy resin (A) or an epoxy resin (C) produced by glycidyl etherification of a bisphenol (I), a novolak resin (II), and a halogenated bisphenol (III) with a halogenated bisphenol (III) for a polyaddition reaction.

Bisphenol (I)

The bisphenol (I) used as a starting material for preparing the epoxy resin (A) or the epoxy resin (C) is a compound represented by the general formula (i):



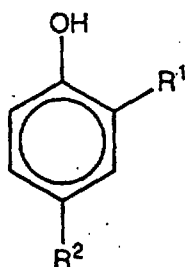
(i),

wherein R is a divalent group selected from the group consisting of $-\text{CH}_2-$, $-\text{CHCH}_3-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{SO}_2-$, , and $-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)-$; R' is independently selected from hydrogen atom and a hydrocarbon containing 1 to 5 carbon atoms; and n is an integer of 0 to 4. Exemplary bisphenols (I) include bisphenol A, bisphenol F, and bisphenol AD. The

most preferred among these is bisphenol A, which is a bisphenol wherein R is isopropylidene group and R' is hydrogen atom in the above formula (i).

Novolak resin (II)

The novolak resin (II) used in preparing the epoxy resin (A) of the present invention or the epoxy resin (C), which is used in the preparation of the epoxy resin composition of the present invention, is a condensation product of formaldehyde and the above-described bisphenol (I) or a phenol represented by the following general formula (ii):



(ii),

wherein R¹ and R² are independently selected from hydrogen atom and a hydrocarbon containing 1 to 10 carbon atoms. Exemplary preferred phenols represented by the general formula (ii) include phenol, o-cresol, p-t-octylphenol, and p-cresol.

The bisphenol (I) which may be condensed with the formaldehyde to produce the novolak resin (II) may be the bisphenol represented by the general formula (i). The bisphenol (I) used for preparing the novolak resin (II) may preferably be bisphenol A or bisphenol AD.

The novolak resin (II) may preferably have a softening point of up to 100°C, and more preferably, a softening point in the range of from 30 to 100°C. When the bisphenol (II) having a softening point in excess of 110°C is used for the epoxy resin preparation, the resulting epoxy resin would not be readily shapable due to an excessively high content of higher molecular weight species, and hence, an excessively high viscosity. When such epoxy resin is further reacted with a halogenated bisphenol (III) to prepare the epoxy resin (B) or (D), the resulting resin would have an excessively high content of higher molecular weight species to result in an insufficient impregnation into the glass cloth.

The novolak resin (II) may preferably have a number average molecular weight of from 300 to 1,000, and more preferably, from 300 to 700, and further preferably, from 350 to 600. Preferably, the novolak resin (II) may also have a molecular weight distribution of up to 2, and most preferably, from 1.1 to 1.8. The term, molecular weight distribution used in the present invention designates the ratio of weight average molecular weight to number average molecular weight, i.e. M_w/M_n .

The novolak resin (II) may be produced by reacting the above-described bisphenol and/or phenol with the formaldehyde either under conditions without or within a solvent such as xylene or toluene, and in the presence of an acidic catalyst. Paraformaldehyde may be used instead of the formaldehyde. The formaldehyde may be used in an

amount of from 0.2 to 0.8 mole per 1 mole of the total of the bisphenol and/or phenol to optimize the softening point and the average molecular weight.

When a solvent is used in the above described reaction, it may be used in a proportion of from 20 to 100% by weight per 100% by weight of the total of said bisphenol and/or phenol.

The acidic catalyst used may typically be a mineral acid such as sulfuric acid, hydrochloric acid, nitric acid, or phosphoric acid; or an organic acid such as p-toluenesulfonic acid or oxalic acid. Among these, p-toluenesulfonic acid is preferred in view of its high acidity and good compatibility with the reaction substrates. The acidic catalyst may be preferably used in a proportion of from 0.05 to 2% by weight, and more preferably, from 0.1 to 1% by weight per 100% by weight of the total of said bisphenol and/or phenol. An excessively small amount of the acidic catalyst used will result in the failure of the reaction, and hence, failure in producing the novolak resin (II) of the desired molecular weight. An excessively large amount of the acidic catalyst used will lead to a difficulty in controlling the reaction, as well as an excessively high molecular weight of the resulting novolak resin.

The reaction may typically be effected by heating the reaction mixture to a temperature of from 70 to 100°C for a period of from 1.5 to 4 hours and then to a temperature of from 100 to 120°C for dehydration condensation. The

dehydration condensation may be promoted either at reduced pressure or by utilizing azeotropy upon reflux in a solvent such as xylene or toluene and removing the water of condensation. Preferably, the reaction is continued until the water of condensation is no longer generated. The reaction may typically take a period of from 3 to 5 hours.

After the completion of the reaction, an alkaline compound is added to the reaction mixture in an amount stoichiometrically equivalent to the acidic catalyst used to thereby neutralize the acidic catalyst. Typical alkaline compounds which may be used include sodium hydroxide, potassium hydroxide, and triethanolamine morpholine. Alternatively, the neutralization may be carried out by adding a non-aqueous solvent to the reaction mixture to form a uniform solution and then, washing the solution with an aqueous alkaline solution.

When the novolak resin (II) is produced by using a solvent, the solvent used is distilled off to leave the novolak resin.

Polynucleated components contained in the novolak resin (II) having a functionality of 3 or more may preferably constitute 3 to 50% by weight, and more preferably, 5 to 40% by weight of the phenolic components in the bisphenol (I) and the novolak resin (II) to provide the epoxy resin (A) or the bisphenol (I), the novolak resin (II) and the halogenated bisphenol (III) to provide the epoxy resin (C). When such content of the polynuclear components is less than 3% by weight, glass transition

temperature after curing of the resulting epoxy resin would not be sufficiently improved. On the other hand, when the content of the polynucleated components is in excess of 50% by weight, the epoxy resin (B) or (D) produced by subsequently reacting the epoxy resin (A) or (C) with the halogenated bisphenol (III) would have an excessively high molecular weight to result in an insufficient impregnation into the glass cloth.

Halogenated bisphenol (III)

The halogenated bisphenol (III) used as a starting material in preparing the epoxy resin (C) may preferably be a bromated bisphenol. The most preferred are tetrabromobisphenol A, tetrabromobisphenol F, and 1,1-bis(3,5-dibromo-4-hydroxyphenyl)ethane.

Glycidylation

The reaction of the bisphenol (I) and the novolak resin (II) with an epihalohydrin or a methylepihalohydrin to produce the epoxy resin (A); and the reaction of the bisphenol (I), the novolak resin (II), and the halogenated bisphenol (III) with an epihalohydrin or a methylepihalohydrin to produce the epoxy resin (C) may be effected in accordance with various known methods. However, it is preferable to sequentially conduct the etherification step and the dehydrohalogenation step in order to provide the resulting glycidyl etherified epoxy resin (A) or (C) with a reliable quality. The epihalohydrin may preferably be

epichlorohydrin, and the methylepichlorohydrin may preferably be 2-methylepichlorohydrin.

The etherification step may be conducted in the presence of an etherification catalyst in an amount of from 0.1 to 5% by mole per 1 equivalent of the phenolic hydroxyl group in the mixture of the bisphenol (I) and the novolak resin (II), or in the mixture of the bisphenol (I), the novolak resin (II), and the halogenated bisphenol (III). Typical etherification catalysts include tertiary amines such as trimethylamine, triethylamine, etc.; tertiary phosphines such as triphenylphosphine, tributylphosphine, etc.; quaternary ammonium salts such as tetramethylammonium chloride, tetramethylammonium bromide, tetraethylammonium chloride, choline chloride, etc.; quaternary phosphonium salts such as tetramethylphosphonium bromide, tetramethylphosphonium iodide, tetraphenylphosphonium bromide, triphenylpropylphosphonium bromide, etc.; tertiary sulfonium salts such as benzyldibutylsulfonium chloride, benzyldimethylsulfonium chloride, etc.; and inorganic bases such as sodium hydroxide, potassium hydroxide, etc. The preferred among these is tetramethylammonium chloride.

In the etherification step, the reaction is proceeded until at least about 50% by mole, and preferably, at least about 70% by mole of the phenolic hydroxyl group is etherified. Typically, the reaction is carried out at a temperature of from 60 to 110°C for a period of 1 to 12 hours in an inert atmosphere. The content of water in the

system may preferably be kept to not more than 3.0% by weight.

The next dehydrohalogenation step may be conducted in the reaction product from the etherification step comprising a unreacted epihalohydrin. In the reaction, it is preferable to use as a catalyst, the alkaline compounds such as alkaline metal hydroxide as those used in the etherification step. In the dehydrohalogenation step, typically, the alkaline compounds are used in a proportion of 0.5 mole or more, preferably 0.8 mole or more per 1 equivalent amount of phenolic hydroxyl group of the novolac resin (II). Preferably, the alkaline compounds are used in a proportion of up to 1 mole per 1 equivalent amount of phenolic hydroxyl group to inconvenience ssuch as gelation of reaction product. The reaction may be conduct generally at a temperature of from 60 to 100°C for 1 to 3 hours. When sodium hydroxide was used, it is preferable that the reaction is carried out by removing the water of by-product. Removing the water may be carried out by dehydrating the reaction mixture, for example, by azeotropy of the epihalohydrin-water, and restoring epihalohydrin to the reaction system. After the completion of the reaction, the epoxy resin of the present invention may be prepared after a post-treatment such as removing unreacted epihalihydrin by vacuum distillation, removing a by-product sallts by treatment such as water washing, and optionally posttreatment such as neutralizing of reaction mixture by weak acid such as phosphoric acid, or sodium

dihydrogenphosphate may be carried out, and filtration and drying. Furthermore, if it is necessary to reduce a amount of hydrolyzable chlorine, second dehydrohalogenation may be carried out again. Alkaline compounds are used to reduce a amount of hydrolyzable chlorine in a proportion of 1 to 3 mole, preferably 1.2 to 3 mole per 1 mole of residue of hydrolyzable chlorine. This reaction may be conducted at a temperature of 60 to 100 °C for a period of about 1 to 3 hours. The reaction may be carried out without or within a solvent. On using a solvent, the preferred is xylene, toluene, MEK, methyl isobutyl ketone.

In the production of the epoxy resin (A), the bisphenol (I) and the novolak resin (II) are used in a weight ratio of 1 to 99 : 99 to 5, preferably, 5 to 95 : 95 to 5, and more preferably, 10 to 90 : 90 to 10. When the novolak component is excessively used, the resulting epoxy resin will have an excessively high content of higher molecular weight species for example, will not sufficiently impregnate into the glass cloth upon fabrication of the prepreg and as a consequence, the resulting laminate will have a poor impact resistance. When the proportion of the novolak resin (II) is excessively low, the resulting epoxy resin will have an insufficient heat resistance.

For the composite materials of heat resistance, the bisphenol (I) and the novolak resin (II) are used in a weight ratio of 50 to 90 : 50 to 10, and preferably, in a weight ratio of 65 to 90 : 35 to 10. When the proportion of the novolak resin (II) is excessively low, the resulting

epoxy resin will have an insufficient heat resistance. When the novolak component is excessively used, the resulting epoxy resin will have an excessively high viscosity and will not be readily shapable.

In the production of the epoxy resin (C), the bisphenol (I), the novolak resin (II) and the halogenated bisphenol (III) are used in a weight ratio of 5 - 80 : 94 - 5 : 1 - 15, preferably 7 - 80 : 90 - 10 : 3 - 10.

The glycidyl etherified epoxy resin (A) produced by the above-described reaction has a epoxy equivalent of from 170 to 220 g/eq and for a printed wiring board, preferably, it has a softening point of up to 50°C, an epoxy equivalent of from 170 to 220 g/eq, a halide content of up to 0.1% by weight. The glycidyl etherified epoxy resin (C) produced by the above-described reaction has a softening point of up to 40°C, an epoxy equivalent of from 170 to 220 g/eq, a halide content of up to 10% by weight.

Polyaddition reaction

The polyadduct resins (B) and (D) which are respectively the main component of the epoxy resin composition of the present invention are manufactured by respectively reacting the epoxy resins (A) and (C) with the halogenated bisphenol (III).

The polyaddition reaction of the epoxy resin (A) or the epoxy resin (B) with the halogenated bisphenol (III) is effected at a temperature of from 120°C to 170°C for 4 to 15 hours in an inert atmosphere in the optional presence of

a catalyst such as a quaternary ammonium salt or a quaternary sulfonium salt in an amount of 10 to 300 ppm.

The reaction may be conducted in a solvent such as toluene, xylene and cyclohexanone such that the solid content in the reaction mixture would be up to 30% by weight.

The halogenated bisphenols (III) which may be used for the polyaddition reaction may be the same as those used for the glycidyl etherification. Among such halogenated bisphenols (III), the preferred are bromated bisphenols, and particularly, tetrabromobisphenol A, tetrabromobisphenol F, and 1,1-bis(3,5-dibromo-4-hydroxyphenyl)ethane.

In the reaction of the epoxy resin (A) with the halogenated bisphenol (III) to produce the polyadduct epoxy resin (B), the epoxy resin (A) and the halogenated bisphenol (III) may preferably be used in a ratio of 74:26 to 55:45. In the reaction of the epoxy resin (C) with the halogenated bisphenol (III) to produce the polyadduct epoxy resin (D), the epoxy resin (C) and the halogenated bisphenol (III) may preferably be used in a ratio of 90:10 to 58:42. When an excessive amount of the halogenated bisphenol (III) is used, higher molecular weight species will be excessively produced to result in a resin composition which will not sufficiently impregnate into the cloth upon fabrication of the prepreg. When the proportion of the halogenated bisphenol (III) is excessively low, the resulting epoxy resin composition will not have a sufficient flame retardancy.

The polyaddition reaction may be effected in the presence of a general-purpose epoxy resin and/or an epoxydized halogenated bisphenol prepared by glycidyl etherifying the above-described halogenated bisphenol (III) with an epihalohydrin or a methylepihalohydrin. When the polyaddition reaction is effected in the presence of the epoxydized halogenated bisphenol, it may preferably be used in a proportion of 1 to 15% by weight per 100% by weight of the total content to prevent coloring of the laminate upon heating.

The epoxy resin composition of the present invention mainly comprising the polyadduct resin (B) prepared by reacting the epoxy resin (A) with the halogenated bisphenol (III) as described above has an epoxy equivalent of from 300 to 500 g/eq, a number average molecular weight, M_n of from 500 to 1,000, a M_n/M_w ratio of 1.7 to 3.0, a halide content of from 15 to 25% by weight, and a content of polyfunctional components of 3 to 40% by weight. It is a viscous product having a narrow molecular weight distribution with a small content of both lower and higher molecular weight species.

The epoxy resin composition of the present invention mainly comprising the polyadduct resin (D) prepared by reacting the epoxy resin (C) with the halogenated bisphenol (III) as described above has an epoxy equivalent of from 300 to 500 g/eq, a number average molecular weight, M_n of from 500 to 1,000, a M_n/M_w ratio of 1.5 to 2.5, a halide content of from 15 to 25% by weight, and a content of

polyfunctional components of 3 to 40% by weight. It is a viscous product having a narrow molecular weight distribution with a small content of both lower and higher molecular weight species.

When the epoxy resin composition of the invention is cured with a curing agent such as dicyanedi- amide or a phenolic novolak resin, the resulting cured product has an improved blister resistance as well as a glass transition temperature, T_g about 10°C higher than that of the cured product of the epoxy resin prepared by using conventional epoxy resins other than the epoxy resin (A) or (C) of the invention. Also, the epoxy resin composition of the present invention exhibits good impregnation into the glass cloth.

As described above, glycidyl etherified epoxy resin (A) or (C) is used in the preparation of the epoxy resin composition of the invention. In the preparation of the epoxy resin composition of the invention, the epoxy resin (A) or (C) may be used either alone or in combination with another epoxy resin having two or more epoxy radicals in one molecule. Exemplary such additional epoxy resins include bisphenol-A epoxy resin, phenolic novolak epoxy resin, cresol novolak epoxy resin and other glycidyl etherified epoxy resins, glycidyl ester epoxy resins, glycidyl amine epoxy resins, linear aliphatic epoxy resins, alicyclic epoxy resins, heterocyclic epoxy resins, halogenated epoxy resins, and other polyfunctional epoxy

resins. Such additional epoxy resins may be used in an amount of up to 50% by weight per 100% by weight of the total epoxy contents, namely, total of the epoxy resin and the additional epoxy resin. When an excessive amount of the additional epoxy resin is used, the resulting composition will no longer have the properties characteristic to the composition of the present invention.

The curing agent used in combination with the epoxy resin composition of the present invention is not limited to any particular type. Typical curing agents are acid anhydrides, aromatic polyamines, aliphatic polyamines, imidazols, and phenolic resins.

Exemplary acid anhydrides include phthalic anhydride, hexahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methylhexahydrophthalic anhydride, methylnadic anhydride, methylnaphthalenedicarboxylic acid, pyromellitic anhydride, trimellitic anhydride, benzophenonetetracarboxylic anhydride, dodecylsuccinic anhydride, chlorendic anhydride, and chloronorbornenedicarboxylic anhydride.

Exemplary aromatic polyamines include diaminodiphenylmethane, diaminodiphenyl sulfone, and amine adducts.

Exemplary aliphatic polyamines include triethylenetetramine, diethylenetriamine, menthenediamine, N-aminoethylpiperadine, isophoronediamine, 3,9-bis(3-aminopropyl)-2,4,8,10-tetraspiro[5,5]undecane, amine adducts.

Exemplary imidazoles include 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 2-

undecylimidazole, 2-ethyl-4-methylimidazole azine, and 1-benzyl-2-methylimidazole.

Exemplary phenol resins include phenolic novolak resins and alkyl-substituted phenolic novolak resins.

Curing agents such as dicyanedi-amine, m-xylylenediamine may also be used in the present invention.

In the present invention, the curing agents as mentioned above may be used either alone or in combination of two or more.

The curing agent may be used with a curing accelerator. Exemplary curing accelerators include imidazoles as mentioned above, for example, 1-benzyl-2-methylimidazole and 2-ethyl-4-methylimidazole; amines such as tertiary amines, for example, N,N-benzyl-dimethylamine and 2,4,6-tris(dimethylaminomethyl)phenol; and tertiary phosphines such as triphenylphosphine.

Other exemplary curing accelerators are 1,8-diazabicyclo-[5,4,0]-undecene-7 octylate, complex compound of monoethylamine and trifluoroboron, and the compound commercially available from Sun Abbot Inc. with the trade name Ucat SA102.

In the present invention, the curing accelerators may be used alone or in combination of two or more.

The epoxy resin composition of the present invention may be blended with a solvent such as acetone, methylethylketone, toluene, xylene, methylisobutylketone, ethyl acetate, ethyleneglycol monomethylether, N,N-dimethylformamide, N,N-dimethylacetoamide, methanol,

ethanol, and the like, which may be used alone or in combination of two or more as a mixed solvent.

The epoxy resin composition of the present invention may optionally contain other additives such as a flame retardant and a filler in accordance with the intended use of the composition.

The epoxy resin composition of the present invention is quite adequate for fabricating a copper clad epoxy resin laminate in accordance with conventional methods. In typical fabrication of the copper clad epoxy resin laminate using the epoxy resin composition of the present invention, the epoxy resin is first dissolved in a solvent to prepare a varnish, and a reinforcement such as a glass cloth is impregnated and/or applied with the thus prepared varnish and dried at an elevated temperature to remove the solvent and produce a prepreg. Next, a copper clad is disposed on one or both surfaces of the prepreg which is used as a single sheet or as a stack of prepreg sheets, and the epoxy resin composition is allowed to cure by applying heat and pressure in accordance with conventional methods.

The present invention is described in further detail by referring to the following Examples and Comparative Examples. It should be noted that the Examples by no means limit the scope of the present invention.

EXAMPLES

In the following Examples and Comparative Examples, viscosity, flexural strength, flexural modulus, and

deflection temperature under load were evaluated as described below.

Viscosity

Viscosity was measured with E-type viscometer at a temperature of 25°C.

Flexural Strength and Flexural Modulus

Test samples having a size of 4 mm x 10 mm x 97 mm were evaluated in accordance with JIS K6911 using Tensilon manufactured by TOYO BALDWIN at a crosshead speed of 1 mm/min using a cell of a maximum load of 500 kg.

Deflection Temperature under Load

Test samples having a size of 12.5 mm x 12.5 mm x 125 mm were evaluated in accordance with JIS K6911 using an apparatus manufactured by Tester Industry K.K.

Synthesis Example 1

Synthesis of a novolak resin using bisphenol A as a phenol

A 1-liter separable flask equipped with a condenser, a thermometer, a stirrer, and a dropping container was charged with 456 g of bisphenol A and 335 g of toluene, and the contents were heated under agitation. When the temperature in the flask reached 70°C, 2.52 g of oxalic acid dihydrate was added as a catalyst. When the temperature in the flask reached 90°C, 82.7 g of 37% aqueous formalin was added dropwise for 2 hours. The contents were agitated for another 1 hour under reflux. The temperature of the contents were further raised to remove water and toluene from the system. When the

temperature reached 150°C, the contents were concentrated for 1 hour at normal temperature, and further concentrated for 1 hour at a reduced pressure of 20 mmHg to obtain a bisphenol A novolak resin (hereinafter referred to as novolak resin (1)). Softening point of the novolak resin (1) evaluated with an automatic softening point-measuring apparatus manufactured by Mettler Inc. was 93°C. The novolak resin was also evaluated for its hydroxyl equivalent in accordance with JIS K0070, and it was 120 g/eq. It had, also, number-average molecular weight of 450; molecular-weight distribution of 1.50.

Example 1

A reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer was charged with 400 g of bisphenol A, 100 g of o-cresol novolak resin (OCN 80 manufactured by Nippon Kayaku K.K.; softening point, 80°C; hydroxyl equivalent 139 g/eq; number-average molecular weight, 425; molecular-weight distribution, 1.30), 1956 g of epichlorohydrin, and 39 g of water. The temperature of the contents was elevated to 65°C. When the reaction mixture became a uniform solution, 23.1 g of 50% aqueous tetramethylammonium chloride was added and allowed to react for 3 hours under agitation.

Next, 331.5 g of 48% aqueous NaOH was added dropwise to the mixture for 2 hours at 70°C and at a reduced pressure, and excessive water was removed from the system by utilizing azeotropy of epichlorohydrin and water to

retain water content in the reaction system at 2% by weight. The epichlorohydrin which was distilled off with the water was separated from the water and recycled to the reaction system. Conditions in the azeotropic distillation including the extent of pressure reduction and heating were controlled such that the amount of water removed from the system per unit time would equal the sum of the amount of water in the 48% aqueous NaOH added to the reaction system and the amount of water produced in the reaction. After completing the addition of the 48% aqueous NaOH, the reaction system was maintained at the same temperature for another 0.5 hour under agitation.

After the completion of the reaction, unreacted epichlorohydrin and water were distilled off the reaction mixture at a reduced pressure. To the residual mixture were added 750 g of xylene and 75 g of water. The reaction mixture was agitated for 0.5 hour at 80°C, and allowed to stand for separation into xylene and aqueous phases. Analysis of the sample collected from the xylene phase exhibited a hydrolyzable chlorine concentration of 1.45% by weight.

Next, 62 g of 48% aqueous NaOH was added to the xylene phase, and the reaction mixture was agitated at 95°C for 2 hours. After the completion of the reaction, gel contents were removed, and 750 g of 25% aqueous monosodium phosphate was added for neutralization. Water was removed from the resulting neutralized product by utilizing xylene-water azeotropy, and the residual mixture was filtered through a

glass filter to separate inorganic salt in the neutralized product. The filtrate was heated to 150°C at a reduced pressure to remove xylene and produce 680 g of epoxy resin. The thus produced epoxy resin had an epoxy equivalent of 185 g/eq and a hydrolyzable chlorine content of 0.06% by weight.

Example 2

The procedure of Example 1 was repeated except that the amount of bisphenol A used was reduced to 260 g and the o-cresol novolak resin used was replaced with the novolak resin (1) synthesized in referential Synthesis Example 1. There was produced 450 g of epoxy resin having an epoxy equivalent of 190 g/eq and a hydrolyzable chlorine content of 0.05% by weight.

Example 3

80 g of the epoxy resin synthesized in Example 1, 72.6 g of methylhexahydrophthalic anhydride (Liquacid MH-700, manufactured by Shin-Nippon Rika K.K.), and 0.4 g of 1,8-diazabicyclo[5.4.0]-7-undecene octilate (Ucat-102, manufactured by Sun-Abbot Inc.) were mixed at 50°C under agitation to prepare a uniform solution of varnish. The uniform solution had a viscosity at 25°C of 993 cps.

The thus produced uniform solution was poured into molds adapted for fabricating test samples for measuring flexural strength and flexural modulus, and further into molds adapted for fabricating test samples for measuring

deflection temperature under load, and then cured by heating at 120°C for 2 hours, at 150°C for 2 hours, and finally, at 170°C for 4 hours. The thus cured test samples were respectively evaluated for their flexural strength, flexural modulus and deflection temperature under load. The results are shown in Table 1.

Example 4

The procedure of Example 3 was repeated except that the epoxy resin used was replaced with 80 g of the epoxy resin synthesized in Example 2, and the amount of the methylhexahydrophthalic anhydride used was reduced to 70.8 g. The resulting uniform solution had a viscosity at 25°C of 896 cps. The uniform solution was also cured into test samples to evaluate their flexural strength, flexural modulus and deflection temperature under load. The results are shown in Table 1.

Comparative Example 1

The procedure of Example 1 was repeated except that no bisphenol-A was used and only o-cresol novolak resin (OCN 80 manufactured by Nippon Kayaku K.K.) was used in an amount of 584 g to produce 650 g of novolak epoxy resin. The thus produced novolak epoxy resin had an epoxy equivalent of 203 g/eq and a hydrolyzable chlorine content of 0.05% by weight.

Comparative Example 2

The procedure of Example 1 was repeated except that no bisphenol A was used and the o-cresol novolak resin was replaced with 504 g of the bisphenol A novolak resin synthesized in referential Synthesis Example 1 to produce 605 g of novolak epoxy resin. The thus produced novolak epoxy resin had an epoxy equivalent of 197 g/eq and a hydrolyzable chlorine content of 0.06% by weight.

Comparative Example 3

The procedure of Example 3 was repeated except that 16 g of the novolak epoxy resin synthesized in Comparative Example 1, 64 g of bisphenol A type liquid epoxy resin (epoxy equivalent, 188 g/eq), 71.4 g of methylhexahydrophthalic anhydride, and 0.4 g of 1,8-diazabicyclo[5.4.0]-7-undecene octilate (Ucat-102, manufactured by Sun-Abbot Inc.) were used to prepare a uniform solution of varnish. The uniform solution had a viscosity at 25°C of 1946 cps. The thus produced uniform solution was cured into test samples to measure flexural strength, flexural modulus, and deflection temperature under load. The ratio of bisphenol A component to novolak component in the cured product was the same as that of Example 3. The results are shown in Table 1.

Comparative Example 4

The procedure of Example 3 was repeated except that 37.4 g of the novolak epoxy resin synthesized in Comparative Example 2, 42.6 g of bisphenol A type liquid

epoxy resin (epoxy equivalent, 188 g/eq), 69.8 g of methylhexahydrophthalic anhydride, and 0.4 g of 1,8-diazabicyclo[5.4.0]-7-undecene octilate (Ucat-102, manufactured by Sun-Abbot Inc.) were used to prepare a uniform solution of varnish. The uniform solution had a viscosity at 25°C of 3379 cps. The thus produced uniform solution was cured into test samples to measure flexural strength, flexural modulus, and deflection temperature under load. The ratio of bisphenol A component to novolak component in the cured product was the same as that of Example 4. The results are shown in Table 1.

Comparative Example 5

The procedure of Example 3 was repeated except that 80 g of bisphenol A type liquid epoxy resin (epoxy equivalent, 188 g/eq), 71.5 g of methylhexahydrophthalic anhydride, and 0.4 g of Ucat-102 were used to prepare a uniform solution of varnish. The thus produced uniform solution was cured into test samples to measure flexural strength, flexural modulus, and deflection temperature under load. The results are shown in Table 1.

Table 1 Properties of the cured product

	<u>Ex.3</u>	<u>Ex.4</u>	<u>C.E.3</u>	<u>C.E.4</u>	<u>C.E.5</u>
Viscosity at 25°C of the varnish before curing, cps	993	896	1946	3379	-
Flexural strength, kg/mm ²	12.9	12.9	12.0	12.1	11.8
Flexural modulus, kg/mm ²	279	292	280	280	277

Deflection temperature under load, °C	159	164	160	165	140
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C.E.: Comparative Example

Synthesis Examples 2 to 5Synthesis of a novolak resins

A 1-liter separable flask equipped with a condenser, a thermometer, a stirrer, and a dropping container was charged with 456 g of bisphenol A and 335 g of toluene, and the contents were heated under agitation. When the temperature in the flask reached 70°C, 2.52 g of oxalic acid dihydrate was added as a catalyst. When the temperature in the flask reached 90°C, 130 g of 37% aqueous formalin was added dropwise for 2 hours, and the reaction was allowed to proceed for another 1 hour under reflux and under agitation. Next, temperature of the system was elevated to remove water and toluene from the system. When the temperature reached 150°C, the contents were concentrated for 1 hour at normal temperature, and further concentrated for 1 hour at a reduced pressure of 20 mmHg to obtain a novolak resin containing residual bisphenol A, which is hereinafter referred to as novolak resin (2). The resulting novolak resin (2) was evaluated for its softening point with an automatic softening point measuring apparatus produced by Mettler Inc. The resin was also evaluated for its residual content of the bisphenol A monomer as well as its number average molecular weight and molecular weight distribution (Mw/Mn) by gel permeation chromatography

(GPC). In the evaluation of the residual content of the bisphenol A monomer, 2 columns of Shim-pack-HSG 10 (manufactured by Shimadzu Seisakusho Ltd.) and 1 column each of Shim-pack-HSG 15 and 20 were connected in series to constitute the separation column. In the evaluation of the molecular weight, HSG-20, 40, 50, and 60 were connected in series. Tetrahydrofran was used for the eluting solution. The molecular weight distribution was measured as described below. The results are shown in Table 2.

The procedure of the above described referential Synthesis Example 2 was repeated except that the bisphenol A, oxalic acid dihydrate, and 37% aqueous formalin were used in the amount shown in Table 2 to produce novolak resins (3) to (5). The thus produced novolak resins (3) to (5) were also evaluated for their softening point, residual content of the bisphenol A monomer, number average molecular weight, and molecular weight distribution. It should be noted that the Synthesis Example 5 is a case wherein 324 g of o-cresol is used instead of the bisphenol A.

Table 2

	<u>Novolak resin</u>			
	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>(5)</u>
<u>Weight of starting materials charged, g</u>				
Bisphenol-A	456	456	456	-
o-cresol	-	-	-	324
Oxalic acid dihydrate	2.52	2.52	2.52	3.8

37% Formalin	130	82.7	33.1	174
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Properties of the resulting product

Softening point, °C	110	93	72	80
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Residual bisphenol-A monomer content, % by weight				
---	--	--	--	--

	22	39	57	23*
--	----	----	----	-----

Number average molecular weight				
---------------------------------	--	--	--	--

	556	450	374	425
--	-----	-----	-----	-----

Molecular weight distribution, Mw/Mn				
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	1.68	1.50	1.12	1.30
--	------	------	------	------

* content of di-nucleic form o-cresol

Synthesis Examples 6 to 15

Synthesis of glycidyl etherified epoxy resins (co-glycidylation)

A 2-liter round flask equipped with a thermometer, a stirrer, a separator, a condenser, and a dropping container was charged with 200 g of novolak resin (2) having a residual content of the bisphenol-A monomer of 22% by weight and 1206 g of epichlorohydrin, and the contents were heated to a temperature of 90°C under agitation. At a temperature of 90°C, 30 g of water and 3 g of tetramethylammonium chloride were added and the mixture was agitated for 4 hours. The temperature of the mixture was reduced to 70°C and the pressure was reduced to 500 mmHg, and at this pressure, 137 g of 48% aqueous solution of sodium hydroxide was added to the mixture from the dropping container for 3 hours, while water was removed from the system with the separator. The water removal was continued

for another 30 minutes after the completion of the dropwise addition of the sodium hydroxide. Pressure of the system was then reduced to 20 mmHg, and the mixture was condensed for 1 hour at 120°C. The pressure was then restored to normal pressure, and 350 g of water and 250 g of toluene were added to the mixture, and the resulting mixture was agitated for 30 minutes at 90°C. The mixture was allowed to stand to thereby promote separation and to remove the thus separated aqueous layer, and the remaining resinous layer was concentrated at 20 mmHg and at 150°C to obtain 264 g of glycidyl etherified epoxy resin, which is hereinafter referred to as epoxy resin (6).

The thus produced epoxy resin (6) was evaluated for its epoxy equivalent by hydrochloric acid-dioxane method. The epoxy resin (6) was also evaluated for its softening point with an automatic softening point measuring apparatus produced by Mettler Inc., and for its composition by gel permeation chromatography (GPC) as in the case of Synthesis Examples 2 to 5. The results are shown in Table 3.

The procedure of Synthesis Example 6 was repeated except that the novolak resin, bisphenol A, epichlorohydrin, and 48% aqueous NaOH were used in the amounts shown in Table 3 to produce epoxy resins (7) to (15). The resulting epoxy resins (7) to (15) were also evaluated for their epoxy equivalent, softening point, and composition. The results are also shown in Table 3.

Table 3

	<u>Epoxy resin</u>									
	<u>(6)</u>	<u>(7)</u>	<u>(8)</u>	<u>(9)</u>	<u>(10)</u>	<u>(11)</u>	<u>(12)</u>	<u>(13)</u>	<u>(14)</u>	<u>(15)</u>
<u>Weight of starting materials charged, g</u>										
Novolak resin (2)	200				50					
(3)		200				93.8	50			
(4)			200					91	230	
(5)				240						60
Bisphenol A					200	106	200	159	25.5	240
Epichlorohydrin	1206	1233	1233	1278	1406	1268	1406	1394	1386	1205
48% NaOH	137	137	137	142	170	141	170	169	168	204
<u>Properties of the resulting glycidylated epoxy resin</u>										
Epoxy equivalent, g/eq	209	197	199	203	182	190	180	183	182	182
Softening point, °C	62	41	viscous	50	viscous	viscous	viscous	viscous	viscous	viscous
Content of n=0 component in the resin*, %	22	30	63	21	90	67	92	82	67	75

* content of bisphenol A diglycidyl ether monomer

Synthesis Examples 16-27Synthesis of polyadduct resins

A 1-liter separable flask equipped with a stirrer and a thermometer was charged with 171 g of bisphenol A epoxy resin (epoxy equivalent, 188 g/eq), 29.4 g of epoxy resin (6) produced in Synthesis Example 6, and 94.3 g of tetrabromobisphenol A, and the contents were heated under agitation. When the temperature was reached 100°C, 0.2 g of tetraethylammonium chloride was added, and the reaction was promoted at 160°C for 5 hours to obtain a polyaddition resin, which is hereinafter referred to as polyadduct resin (16).

The polyadduct resin (16) was evaluated for its epoxy equivalent by the same method as described above. The resin was also evaluated for its number average molecular weight by gel permeation chromatography (GPC) using the column of Shim-pack-HSG 20, 40, 50 and 60 connected in series, and for its molecular weight distribution by the same method as described above.

The procedure of Synthesis Example 16 was repeated except that the epoxy resin, bisphenol A epoxy resin, and tetrabromobisphenol A were used in the amounts shown in Table 4 to produce polyadduct resins (17) to (25). The polyadduct resins (17) to (25) were also evaluated for their epoxy equivalent, number average molecular weight, and molecular weight distribution.

The procedure of Synthesis Example 16 was also repeated except that the tetrabromobisphenol A was replaced with tetrabromobisphenol A epoxy resin in the amount shown in Table 4, and the epoxy resin and the bisphenol A epoxy resin were used in the amounts shown in Table 4 to produce polyadduct resins (26) and (27). The polyadduct resins (26) and (27) were also evaluated for their epoxy equivalent, number average molecular weight, and molecular weight distribution.

Table 4

		<u>Polyadduct resin</u>											
		<u>(16)</u>	<u>(17)</u>	<u>(18)</u>	<u>(19)</u>	<u>(20)</u>	<u>(21)</u>	<u>(22)</u>	<u>(23)</u>	<u>(24)</u>	<u>(25)</u>	<u>(26)</u>	<u>(27)</u>
<u>Weight of starting materials charged, g</u>													
Epoxy resin	(6)	29.4											
	(10)					147						150	
	(7)		42.1										
	(11)						83.6						85
	(12)							147					
	(8)			57.7									
	(13)								200				
	(14)									200			
	(9)				37								
	(15)										147		
Bisphenol A epoxy resin*		171	158	142	163	52.9	116	52.9			53	25	111
Tetrabromobisphenol A		94.3	94.3	94.3	94.3	94.3	94.3	94.3	92.5	92.5	94.3		
Tetrabromobisphenol A epoxy resin												64	81.7
<u>Properties of the resulting polyadduct resin</u>													
Epoxy equivalent, g/eq		436	424	390	425	401	419	400	402	384	410	391	381
Number average MW		737	763	589	745	678	761	655	589	749	677	650	735
MW distribution		3.21	2.07	1.88	1.93	2.20	1.99	1.87	1.88	2.21	1.83	1.91	1.92

* Bisphenol A epoxy resin having an epoxy equivalent of 188 g/eq.

** Tetrabromobisphenol A epoxy resin: EPICLON 152-S manufactured by Dainippon Ink & Chemicals, Inc. having a softening point of 62°C, an epoxy equivalent of 364 g/eq, and a bromine content of 47.6 wt%.

Example 5

To a solution of 100 g polyadduct resin (20) in 25 g methylethylketone was added a solution of 2.5 g dicyanedi-
amide and 0.15 g 2-ethyl-4-methylimidazole in 20 g ethylene glycol monomethyl ether to produce a varnish of an epoxy resin composition. A glass cloth (WEA-18W105F manufactured by Nitto Boseki Co., Ltd.) was impregnated with the thus produced varnish, and then dried in a drying furnace at 140°C for 6 minutes to prepare a prepreg. The prepreg had a content of the epoxy resin composition of 49% by weight.

The prepreg was evaluated for its appearance.

The prepreg was crumpled to collect the epoxy resin composition, and the thus collected epoxy resin composition was placed in a mold adapted for fabricating a test sample sheet of 1 mm thick. The test sample sheet was placed in Reolosolid manufactured by Toyobo Co, Ltd. to evaluate the epoxy resin composition for its glass transition temperature, T_g at a temperature elevation rate of 2°C/min.

The prepreg was also fabricated into a laminate by stacking four sheets of the prepreg and press-molding the stack at 170°C for 1 hour at a pressure of 20 kg/cm². The laminate was immersed in water at a temperature of 121°C and at a pressure of 2 kg/cm² for a predetermined period of time, and then, immersed in a soldering bath at 260°C for 20 seconds. The laminate was evaluated for its resistance to soldering heat after pressure cooker test (PCT) in accordance with the following criteria:

- O: no blister or ply separation,
- Δ: few blisters or slight ply separation, and
- x: many blisters or considerable ply separation.

The results are shown in Table 5.

Examples 6 to 12

The procedure of Example 5 was repeated by substituting the polyadduct resin (20) with the polyadduct resins (21) to (27), respectively as shown in Table 5 to prepare varnishes and then, prepregs. The thus produced varnishes and prepregs were evaluated for their glass transition temperature, resistance to soldering heat after PCT, and impregnation as in the case of Example 5. The results are also shown in Table 5.

Table 5

	<u>Example</u>							
	5	6	7	8	9	10	11	12
<u>Weight of starting materials charged, g</u>								
Polyadduct resin (20)	100							
(21)		100						
(22)			100					
(23)				100				
(24)					100			
(25)						100		
(26)							100	
(27)								100
Dicyanediarnide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
2-ethyl-4-methyl- imidazole	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
<u>Properties of the cured product</u>								
Glass transition temperature Tg, °C	162	163	161	160	169	156	169	168
Resistance to soldering heat after PCT								
120 min	0	0	0	0	0	0	0	0
150 min	Δ	0	0	0	0	0	0	0
Impregnation of the varnish into glass cloth								
	fair	good	good	good	good	good	good	good

Comparative Examples 6 to 12

The procedure of Example 5 was repeated except that the epoxy resins (6) to (9) shown in Table 3 and the polyadduct resins (16) to (19) shown in Table 4 were used in the amounts shown in Table 6 to prepare varnishes of the epoxy resin composition, and then, prepregs. The thus produced varnishes and prepregs were evaluated for their glass transition temperature, resistance to soldering heat after PCT, and impregnation as in the case of Example 5. The results are shown in Table 6.

Table 6

	<u>Comparative Example</u>						
	6	7	8	9	10	11	12
<u>Composition of the epoxy resin composition</u>							
Epoxy resin (6)					10		
(7)						10	
(8)							
(9)							10
Polyadduct resin (16)	100						
(17)		100					
(18)			100				
(19)				100			
Bromated bisphenol A epoxy resin*					90	90	90
Dicyanediarnide	2.5	2.5	2.5	2.5	2.5	2.5	2.5
2-ethyl-4-methyl-imidazole	0.15	0.15	0.15	0.15	0.15	0.15	0.15
<u>Properties of the cured product</u>							
Glass transition temperature Tg, °C	157	159	159	157	154	159	157
Resistance to soldering heat after PCT							
120 min	Δ	Δ	0	0	Δ	0	0
150 min	x	x	x	x	x	x	x
Impregnation of the varnish into glass cloth	poor	fair	good	good	fair	good	good

* Bromated bisphenol A epoxy resin having a bromine content of 21% by weight and an epoxy equivalent of 476 g/eq.

Synthesis Examples 28 to 37Synthesis of glycidyl etherified epoxy resins (co-glycidylation)

A 2-liter round flask equipped with a thermometer, a stirrer, a separator, a condenser, and a dropping container was charged with 30.7 g of novolak resin (2) synthesized in Synthesis Example 2, and 171 g of bisphenol A, 17.5 g of tetrabromobisphenol A, and 1178 g of epichlorohydrin, and the contents were heated to a temperature of 90°C under agitation. At a temperature of 90°C, 30 g of water and 3 g of tetramethylammonium chloride were added and the mixture was agitated for 4 hours. The temperature of the mixture was reduced to 70°C, and the pressure was reduced to 500 mmHg, and at this pressure, 142.5 g of 48% aqueous solution of sodium hydroxide was added to the mixture from the dropping container for 3 hours, while water was removed from the system with the separator. The water removal was continued for another 30 minutes after the completion of the dropwise addition of the aqueous solution of sodium hydroxide. Pressure of the system was then reduced to 20 mmHg, and the mixture was condensed for 1 hour at 120°C. The pressure was then restored to normal pressure, and 350 g of water and 250 g of toluene were added to the mixture, and the resulting mixture was agitated at 90°C for 30 minutes. The mixture was allowed to stand to thereby promote separation of aqueous layer and to remove the thus separated aqueous layer, and the remaining resinous layer

was concentrated at 20 mmHg and at 150°C for 1 hour to obtain 1 g of glycidyl etherified epoxy resin, which is hereinafter referred to as epoxy resin (28).

The thus produced epoxy resin (28) was evaluated for its epoxy equivalent by hydrochloric acid-dioxane method. The epoxy resin (28) was also evaluated for its softening point with an automatic softening point measuring apparatus produced by Metler Inc., and for its composition by gel permeation chromatography (GPC) as in the case of Synthesis Examples 2 to 5.

The procedure of Synthesis Example 28 was repeated except that of the novolak resin, bisphenol A, tetrabromobisphenol A, epichlorohydrin, and 48% aqueous NaOH were used in the amounts as shown in Table 7 to produce epoxy resins (29) to (37). The resulting epoxy resins (29) to (37) were also evaluated for their epoxy equivalent, softening point, and composition. The results are shown in Table 7.

Table 7

	Epoxy resin									
	(28)	(29)	(30)	(31)	(32)	(33)	(34)	(35)	(36)	(37)
<u>Weight of starting materials charged, g</u>										
Novolak resin (2)	200			50				30.7		
(3)		200			93.8	50			53.0	
(5)			240				60			59.3
Bisphenol A				200	106	200	240	171	172	166
Tetrabromobisphenol A	-	-	-	-	-	-	-	17.5	20.8	20.8
Epichlorohydrin	1206	1233	1278	1406	1268	1406	1205	1178	1311	1309
48% NaOH	137	137	142	170	141	170	204	143	159	158
<u>Resulting glycidylated epoxy resin</u>										
Epoxy equivalent, g/eq	209	197	203	182	190	180	182	187	190	189
Softening point, °C	62	41	50	viscous	viscous	viscous	viscous	viscous	viscous	viscous
Content of n=0 component in the resin*, %	22	30	21	90	67	92	75	86	82	79

* total content of bisphenol A diglycidyl ether monomer and tetrabromobisphenol-A diglycidyl ether monomer.

Synthesis Examples 38-48Synthesis of polyadduct resins

A 1-liter separable flask equipped with a stirrer and a thermometer was charged with 200 g of epoxy resin (28) prepared in Synthesis Example 28 and 78 g of tetrabromobisphenol A, and the contents were heated under agitation. When the temperature in reached 100°C, 0.2 g of tetraethylammonium chloride was added, and the reaction was promoted at 160°C for 5 hours to obtain a polyadduct resin, which is hereinafter referred to as polyadduct resin (38).

The thus produced polyadduct resin (38) was evaluated for its epoxy equivalent as in the case of Synthesis Example 16. The polyadduct resin (38) was also evaluated for its molecular weight by gel permeation chromatography (GPC) using the column of Shim-pack-HSG 20, 40, 50 and 60 connected in series, and for its molecular weight distribution as in the case of Synthesis Example 16. The results are shown in Table 8.

The procedure of Synthesis Example 38 was repeated except that the epoxy resin, bisphenol-A epoxy resin, and tetrabromobisphenol-A were used in the amounts as shown in Table 8 to produce polyadduct resins (39) to (47). The polyadduct resins (39) to (47) were also evaluated for their epoxy equivalent, number average molecular weight, and molecular weight distribution. The results are also shown in Table 8.

Table 8

	<u>Polyadduct resin</u>									
	<u>(38)</u>	<u>(39)</u>	<u>(40)</u>	<u>(41)</u>	<u>(42)</u>	<u>(44)</u>	<u>(45)</u>	<u>(46)</u>	<u>(47)</u>	<u>(48)</u>
<u>Weight of starting materials charged, g</u>										
Epoxy resin (28)	29.4									
(29)		42.1								
(30)			37							
(31)				147						
(32)					83.6					
(33)						147				
(34)							147			
(35)								200		
(36)									200	
(37)										200
Bisphenol A epoxy resin*	171	158	163	52.9	116	52.9	53			
Tetrabromobisphenol A	94.3	94.3	94.3	94.3	94.3	94.3	94.3	78.0	77.2	77.2
<u>Properties of the resulting polyadduct resin</u>										
Epoxy equivalent, g/eq	436	424	425	401	419	400	410	354	357	356
Number average MW	737	763	745	678	761	655	677	605	616	588
MW distribution	3.21	2.07	1.93	2.20	1.99	1.87	1.8	2.08	1.87	1.69

* Bisphenol A epoxy resin having an epoxy equivalent of 188 g/eq.

Example 13

To a solution of 100 g polyadduct resin (45) in 25 g methylethylketone was added a solution of 2.5 g dicyanedi-
amide and 0.15 g 2-ethyl-4-methylimidazole in 20 g ethylene glycol monomethyl ether to produce a varnish of an epoxy resin composition. A glass cloth (WEA-18W05F manufactured by Nitto Boseki Co., Ltd.) was impregnated with the thus produced varnish, and then dried in a drying furnace at 140°C for 6 minutes to prepare a prepreg. The prepreg had a content of the epoxy resin composition of 49% by weight.

The prepreg was evaluated for its appearance.

Glass transition temperature, T_g was evaluated by using the prepreg as in the case of the Examples 5 to 12. The prepreg was also evaluated for its impregnation and resistance to soldering heat after pressure cooker test (PCT). The results are shown in Table 9.

Examples 14 and 15

The procedure of Example 13 was repeated by substituting the polyadduct resin (45) with the polyadduct resins (46) and (47), respectively in the amount shown in Table 9 to prepare varnishes and then, prepregs. The thus produced varnishes and prepregs were evaluated for their glass transition temperature, resistance to soldering heat after PCT, and impregnation as in the case of Example 13. The results are also shown in Table 9.

Table 9

	<u>Example</u>		
	<u>13</u>	<u>14</u>	<u>15</u>
<u>Composition of the epoxy resin composition</u>			
Polyadduct resin (45)	100		
(46)		100	
(47)			100
Dicyanediarnide	2.5	2.5	2.5
2-ethyl-4-methyl- imidazole	0.15	0.15	0.15
<u>Properties of the cured product</u>			
Glass transition temperature Tg, °C	171	170	162
Resistance to soldering heat after PCT			
120 min	O	O	O
150 min	O	O	Δ
Impregnation of the varnish into glass cloth			
	good	good	good

Comparative Examples 13 to 22

The procedure of Example 13 was repeated except that the epoxy resins (28) to (30) shown in Table 7 and the polyadduct resins (38) to (44) shown in Table 8 were used in the amounts shown in Table 10 to prepare varnishes of the epoxy resin composition and then, prepregs. The thus produced varnishes and prepregs were evaluated for their glass transition temperature, resistance to soldering heat after PCT, and impregnation as in the case of Example 13. The results are shown in Table 10.

Table 10

	<u>Comparative Example</u>									
	13	14	15	16	17	18	19	20	21	22
<u>Composition of the epoxy resin composition</u>										
Epoxy resin (28)				10						
(29)					10					
(30)										
Polyadduct resin (38)	100									
(39)		100								
(40)			100							
(41)							100			
(42)								100		
(43)									100	
(44)										100
Bromated bisphenol A epoxy resin*				90	90	90				
Dicyanediarnide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
2-ethyl-4-methylimidazole	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
<u>Properties of the cured product</u>										
Glass transition temperature Tg, °C	157	159	159	154	159	157	162	163	161	156
Resistance to soldering heat after PCT										
120 min	Δ	Δ	0	Δ	0	0	0	0	0	0
150 min	x	x	x	x	x	x	Δ	0	0	0
Impregnation of the varnish into glass cloth	poor	fair	good	fair	good	good	fair	good	good	good

* Bromated bisphenol A epoxy resin having a bromine content of 21% by weight and an epoxy equivalent of 476 g/eq.

As set forth above, the epoxy resin of the present invention is easy to shape since it exhibits a considerably low viscosity upon mixing with a curing agent. Once cured, the epoxy resin of the present invention exhibits an excellent heat resistance as well as a high mechanical strength. Therefore, it is well suited for use in combination with various types of fibers to constitute plastic composite materials.

The epoxy resin composition comprising as its main component a polyadduct resin prepared by polyaddition reaction of the particular co-glycidyl etherified epoxy resin of the present invention exhibits excellent impregnation into such materials as glass cloth, and once cured, the cured product shows excellent heat resistance, blister resistance, and adhesion to copper clad.

CLAIMS

1. An epoxy resin (A) obtainable by glycidyl etherifying a bisphenol (I) and a novolak resin (II) with at least one member selected from an epihalohydrin and a methylepihalohydrin.
2. An epoxy resin (A) according to claim 1 wherein said bisphenol (I) and said novolak resin (II) are used in a weight ratio of 1 - 95 : 99 - 5.
3. An epoxy resin (A) according to claim 2 wherein said bisphenol (I) and said novolak resin (II) are used in a weight ratio of 50 - 90 : 50 - 10.
4. An epoxy resin (A) according to any one of claims 1 to 3 wherein said novolak resin (II) has a softening point of up to 110°C, a number average molecular weight of 1,000 to 300, and a molecular weight distribution of up to 2.
5. A process for producing an epoxy resin (A) which comprises glycidyl etherifying a bisphenol (I) and a novolak resin (II) as defined in any one of claims 1 to 4 with at least one member selected from an epihalohydrin and a methylepihalohydrin.
6. An epoxy resin composition comprising a polyadduct resin (B) obtainable by reacting an epoxy resin (A) as defined in any one of claims 1 to 4 with a halogenated bisphenol (III).
7. An epoxy resin composition according to claim 6 wherein said reaction is conducted in the presence of at least one member selected from an epoxy resin (E) and an epoxydized halogenated bisphenol (F).
8. An epoxy resin composition according to claim 7 wherein said epoxydized halogenated bisphenol (F) is used in an amount of 1 to 15% by weight.
9. A process for preparing a polyadduct resin (B) which comprises reacting an epoxy resin (A) as defined in any one of claims 1 to 4 with a halogenated bisphenol (III).
10. A process according to claim 9 which is conducted in the presence of at least one member selected from an epoxy resin (E) and an epoxydized halogenated bisphenol (F).
11. A varnish comprising as its main components a



solvent and an epoxy resin composition as defined in any one of claims 6 to 8.

12. A prepreg or laminate comprising a reinforcement impregnated with a varnish as defined in claim 11.

13. An epoxy resin composition comprising a polyadduct resin (D) obtainable by glycidyl etherifying a bisphenol (I), a novolak resin (II) and a halogenated bisphenol (III) with at least one member selected from an epihalohydrin and a methylepihalohydrin to produce an epoxy resin (C); and reacting the epoxy resin (C) with a halogenated bisphenol (III).

14. An epoxy resin composition according to claim 13 wherein said reaction between said epoxy resin (C) and said halogenated bisphenol (III) is conducted in the presence of an epoxy resin (E).

15. An epoxy resin composition according to claim 13 or 14 wherein said novolak resin (II) has a softening point of up to 110°C, a number average molecular weight of 1,000 to 300, and a molecular weight distribution of up to 2.

16. An epoxy resin composition according to any one of claims 13 to 15 wherein said bisphenol (I), said novolak resin (II) and said halogenated bisphenol (III) are used in a weight ratio of 5 - 80 : 94 - 5 : 1 - 15.

17. A process for producing a polyadduct resin (D) which comprises reacting an epoxy resin (C) as defined in claim 13 with a halogenated bisphenol (III).

18. A process according to claim 17 which is conducted in the presence of an epoxy resin (E).

19. A varnish comprising as its main components a solvent and an epoxy resin composition as defined in any one of claims 13 to 16.

20. A prepreg or laminate comprising a reinforcement impregnated with a varnish as defined in claim 19.

21. An epoxy resin or epoxy resin composition substantially as described in any one of Examples 1 to 4.

22. A varnish substantially as described in any one of Examples 5 to 15.



23. A prepreg substantially as described in any one of Examples 5 to 15.

