[DESCRIPTION]

[TITLE OF INVENTION]

EPOXY RESIN, CURABLE RESIN COMPOSITION, AND CURED OBJECT THEREFROM

[Technical Field]

[0001]

The present invention relates to an epoxy resin having a specific structure, a curable resin composition, and a cured object therefrom.

[Background Art]

[0002]

Since epoxy resins have excellent electrical properties (dielectric constant/dielectric loss tangent, insulating properties), mechanical properties, adhesive properties, and thermal properties (such as heat resistance), they are widely used in the electrical and electronic fields such as in cast products, laminated substrates, and IC encapsulation materials and in the fields of structural materials, adhesives, paints and the like.

[0003]

In recent years, in the electrical and electronic fields, improvement of performance such as flame retardancy, moisture resistance, adhesion, and dielectric properties of resin compositions, and further improvement of various properties such as high purity, low viscosity for highly-filled fillers (inorganic or organic fillers), and improvement in reactivity for shortening the molding cycle (Patent Literature 1) have been required. In addition, as structural materials, lightweight materials with excellent mechanical properties are required for aerospace materials, leisure and sport device applications and the like.

[0004]

In the field of semiconductor encapsulation, as semiconductors have changed, substrates (substrates themselves or their surrounding materials) have become thinner, stacked, systemized, three-dimensionalized, and complicated, and now require properties such as very high levels of heat resistance and high fluidity. In particular, with the expansion of automotive applications for plastic packages, the demand for improved heat resistance has become even more stringent. Specifically, due to an increase in driving temperature of semiconductors, very high heat resistance is required, and in recent years, there has also been a movement to shift to high-wide-gap semiconductors, and it has become necessary to deal with the driving temperatures of 175°C and also 200°C or higher. For these driving temperatures, sufficient heat resistance (glass transition temperature (Tg), particularly Tg in thermomechanical properties (TMA)) is required for peripheral members. Specifically, a temperature about 10% higher than the driving temperature is required (at 200°C, a Tg of 220°C or higher, for example, 225°C is required), and the demand is increasing year by year (Non-Patent Literature 1).

[0005]

In addition, in recent years, amid the need for electric vehicles, the need for high-voltage power devices has increased rapidly, and tracking resistance properties have come to be considered important. In addition, in applications such as solar power generation, wind power generation, and EVs, tracking resistance properties are considered important, and a comparative tracking index (CTI) greater than 600 is required for particularly demanding applications.

[Citation List]

[Patent Literature]

[0006]

[Patent Literature 1]

Japanese Patent Laid-Open No. 2019-001841

[Non-Patent Literature]

[0007]

[Non-Patent Literature 1]

Fuji Electric Journal, 2016 vol. 89 No. 4, pp. 247-250

[Summary of Invention]

[Technical Problem]

[0008]

Generally, an aromatic crosslinking unit is sometimes introduced in order to improve heat resistance of a resin composition, but in this case, since the main framework is aromatic, it is easily carbonized, and tracking resistance properties deteriorate. In addition, when the heat resistance is improved by increasing the molecular weight, the thermal decomposition temperature increases due to the increase in the molecular weight, and the tracking resistance properties deteriorate. That is, since the heat resistance and tracking properties have a trade off relationship, it is very difficult to satisfy having these tracking properties while maintaining heat resistance. In addition, when a resin containing a polysensitive aromatic compound is added in order to impart properties such as flame retardancy, the tracking resistance properties tend to deteriorate, and it is difficult to achieve both improved tracking resistance properties and flame retardancy.

Generally, a performance level category (PLC) is set according to the CTI value. Since the PLC belongs to a smaller class, the design size (creepage distance) of the device can be reduced, and thus the PLC is preferably 3 or less and particularly preferably 1 or less.

Here, the PLC and the CTI have the following relationship.

PLC 1: CTI 600 or more, PLC 2: CTI 400 or more and less than 600, PLC 3: 250 or more and less than 400, PLC 4: 100 or more and less than 175, PLC 5: less than 100.

[0009]

The present invention has been made in view of the above circumstances, and an objective of the present invention is to provide an epoxy resin and a curable resin composition from which a cured object has excellent heat resistance and tracking resistance properties.

[Solution to Problem]

[0010]

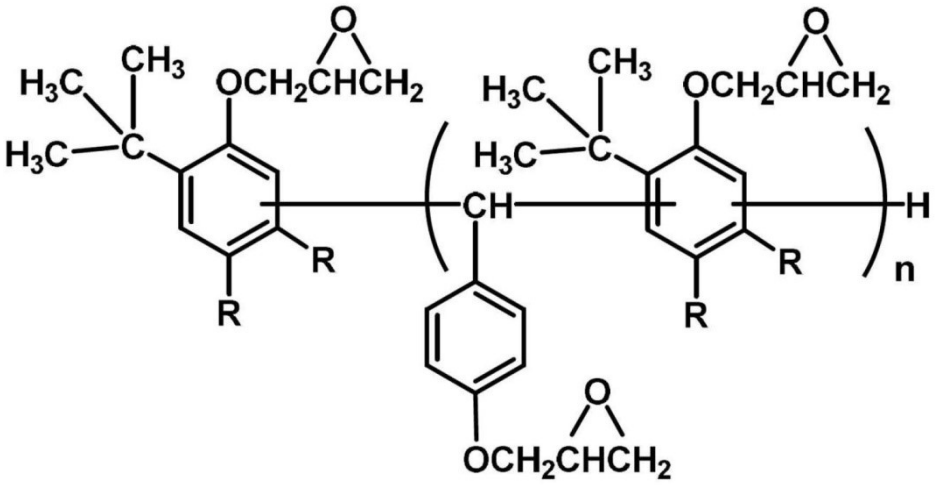
The inventors conducted extensive studies in order to address the above problems, and as a result, completed the present invention. That is, the present invention relates to the following [1] to [3]. Here, in this specification, "(numerical value 1) to (numerical value 2)" indicates that upper and lower limit values are included.

[1]

An epoxy resin represented by the following Formula (1) and having a value obtained by dividing the epoxy equivalent (g/eq.) by a softening point (°C) of 2.0 or more and less than 2.2:

[0011]

[Chem. 1]



(1)

[0012]

(in Formula (1), a plurality of R's are present independently and each represents a methyl group or a hydrogen atom, and n is an average number of repetitions, and a real number of 1 to 10).

[2]

A curable resin composition containing the epoxy resin according to [1].

[3]

The curable resin composition according to [2],

wherein the content of inorganic fillers in a total amount of the curable resin composition is 74 wt% or more and 95 wt% or less.

[4]

A cured object obtained by curing the curable resin composition according to [2] or [3].

[Advantageous Effects of Invention]

[0013]

The present invention relates to an epoxy resin having a specific structure, a curable resin composition and a cured object therefrom, and the cured object has

excellent heat resistance and tracking resistance properties.

Therefore, the present invention is beneficial for various composite materials, adhesives, paints and the like including insulating materials for electric and electronic components (highly reliable semiconductor encapsulation materials, etc.), laminated substrates (printed wiring substrates, build-up substrates, etc.) and CFRP.

[Brief Description of Drawings]

[0014]

Fig. 1 shows GPC charts of Synthesis Example 1.

Fig. 2 shows GPC charts of Synthesis Example 2.

Fig. 3 shows GPC charts of Synthesis Example 3.

Fig. 4 shows GPC charts of Example 1.

Fig. 5 shows GPC charts of Example 2.

Fig. 6 shows GPC charts of Example 3.

Fig. 7 shows GPC charts of Comparative Synthesis Example 1.

Fig. 8 shows GPC charts of Comparative Synthesis Example 2.

Fig. 9 shows GPC charts of FAE-2500.

Fig. 10 shows TMA charts of Examples 4 and 5 and Comparative Examples 1 and 2.

Fig. 11 shows GPC charts of Synthesis Example 4.

Fig. 12 shows GPC charts of Example 7.

Fig. 13 shows CTI measurement results of Examples 10 to 13 and Comparative Examples 5 to 8.

[Description of Embodiments]

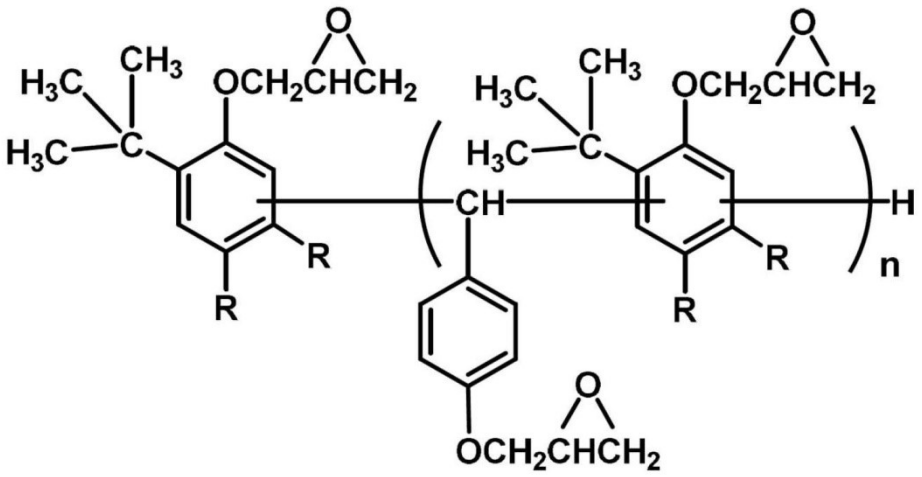
[0015]

An epoxy resin of the present invention is represented by the following Formula

(1) and has a value of 2.0 or more and less than 2.2 that is obtained by dividing an epoxy equivalent (g/eq.) by a softening point (°C).

[0016]

[Chem. 2]



(1)

[0017]

(in Formula (1), a plurality of R's are present independently and each represents a methyl group or a hydrogen atom, and n is an average number of repetitions, and a real number of 1 to 10).

[0018]

In Formula (1), n can be calculated from the number average molecular weight determined by gel permeation chromatography (GPC, detector: UV 254 nm) measurement or from the area ratio of each of separated peaks. n is more preferably a real number of 1 to 5 and particularly preferably a real number of 2 to 4.

[0019]

n=1 in Formula (1) is preferably less than 50 area% and more preferably less than 45 area%. In addition, the lower limit thereof is 25 area%, and if it is less than 25 area%, the fluidity of the resin deteriorates, and productivity deteriorates when the resin

is used as an encapsulation material. The melt viscosity of the resin is an index of fluidity, and the viscosity (ICI melt viscosity) measured by a cone-plate method at 150°C is preferably a viscosity of 2 Pa·s or less. In addition, if the viscosity is too low, there is a possibility of voids caused by entrainment of air during molding, and blocking may occur during adding (or modification) of a liquid resin, and thus the viscosity is preferably 0.4 Pa·s or more. In addition, in consideration of the balance between heat resistance and thermal decomposition properties, the viscosity is more preferably 0.45 Pa·s or more and particularly preferably 0.5 Pa·s or more.

[0020]

In addition, the compound in Formula (1) with n=less than 1 is contained in a proportion of preferably 0.5 to 10 area%, more preferably 0.5 to 5 area%, and particularly preferably 0.5 to 2.5 area%. Since the compound with n=less than 1 is a compound having a structure which is trifunctional or lower or an epoxy resin of tertiary butylmethylphenol, if the amount of the compound with n=less than 1 exceeds 10 area%, not only is a decrease in heat resistance suggested but there is also a concern about odors during handling or an adverse effect on the human body. On the other hand, if the amount of the compound with n=less than 1 is less than 0.5 area%, the network becomes too dense, and thus the weight loss due to thermal decomposition increases, and there is a concern about an adverse effect on thermal decomposition properties (and eventually, it is assumed that tracking properties will be adversely affected).

[0021]

The epoxy resin of the present invention is generally in the form of a solid resin at room temperature, and the softening point thereof is preferably 90°C or higher and more preferably 95°C or higher. In addition, the upper limit thereof is 150°C. If the softening point is higher than 150°C, the solvent tends to remain when the resin is taken

out, and voids tend to occur during curing. In addition, there are major problems in production such as foaming easily when the solvent is distilled off. On the other hand, if the softening point is 90°C or lower, there is an adverse effect on heat resistance and thermal decomposition resistant properties. In addition, the epoxy equivalent is preferably 200 to 300 g/eq., and more preferably 205 to 250 g/eq.. If the epoxy equivalent is less than 200 g/eq., epichlorohydrin remains and a large amount of epoxidized impurities remains, and there is a possibility of properties deteriorating. In addition, if the epoxy equivalent is more than 300 g/eq., there is a problem of heat resistance decreasing.

[0022]

In the present invention, the epoxy equivalent is measured by the method according to JIS K-7236. The softening point is measured using softening point measuring instrument FP90 (commercially available from METTLER TOLEDO).

[0023]

The epoxy resin of the present invention preferably has a high softening point and a large number of functional groups per unit molecular weight. The softening point tends to increase as the molecular weight increases. This means that the softening point indicates the fluidity of the resin when heated, and as the molecular weight becomes larger, molecules are less likely to move, that is, the softening point becomes higher. On the other hand, it is generally said that the heat resistance improves as the softening point increases, but it is more effective to increase the number of functional groups per unit weight in order to increase the heat resistance, and the epoxy equivalent is a value linked to the number of functional groups.

[0024]

It can be understood that, when the softening point is low and the epoxy

equivalent is high, it is suggested that there are few functional groups per molecule, and on the other hand, when the softening point is high and the epoxy equivalent is low, there are many functional groups per molecule. Therefore, a compound having a high softening point and a low epoxy equivalent is preferable.

[0025]

In the present invention, the value obtained by dividing an epoxy equivalent (g/eq.) by a softening point (°C) is defined as the parameter A, and the parameter A is preferably 2.0 or more and less than 2.2. It is thought that, if the parameter A is less than 2.0, some impurities may remain because the epoxy equivalent is too small, and on the other hand, when the parameter A is 2.2 or more, it means that the epoxy equivalent is large and the softening point is low relative to the value of the epoxy equivalent, and it is not possible to achieve both heat resistance and thermal decomposition properties.

[0026]

Here, thermal decomposition properties are said to be a parameter that affects tracking resistance properties, and it is thought that, if the thermal decomposition temperature is lower in the trunking test, it is difficult to conduct electricity between electrodes, and thus it is possible to withstand a high voltage. Generally, it is thought that, when the molecular weight increases, the thermal decomposition temperature tends to increase, but in the present invention, even if the molecular weight increases, there is no large difference in the thermal decomposition temperature, and improved tracking resistance properties can be maintained.

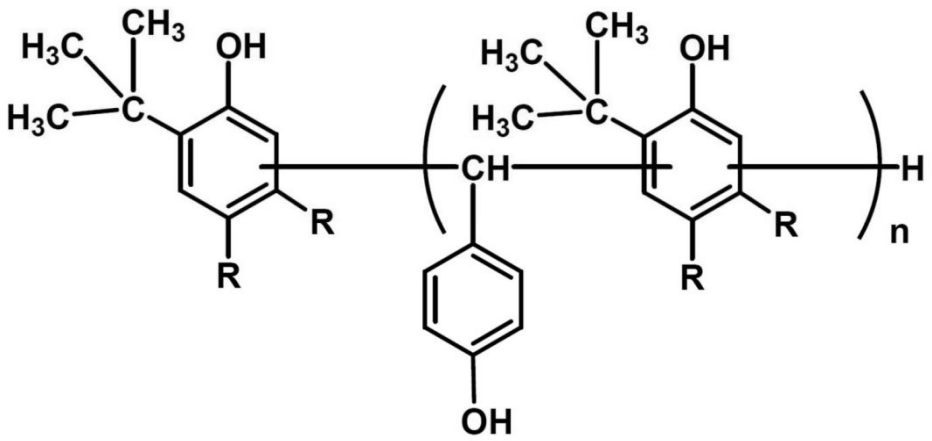
[0027]

A method of producing the epoxy resin of the present invention is not particularly limited, for example, it can be obtained by subjecting the phenolic resin represented by the following Formula (2) and epihalohydrin to an addition or ring-

closure reaction in the presence of a solvent and a catalyst.

[0028]

[Chem. 3]



(2)

[0029]

(in Formula (2), a plurality of R's are present independently and each represents a methyl group or a hydrogen atom, and n is an average number of repetitions, and a real number of 1 to 10).

[0030]

In Formula (2), n can be calculated from the number average molecular weight determined by gel permeation chromatography (GPC, detector: UV 254 nm) measurement or from the area ratio of each of separated peaks. n is more preferably 1 to 5 and particularly preferably 1 to 3.

[0031]

The hydroxyl group equivalent of the phenolic resin of Formula (2) is preferably 140 to 180 g/eq., and more preferably 140 to 165 g/eq.. In addition, the amount of compounds with n=1 is preferably 30 to 60 area% and more preferably 40 to 60 area%. In addition, a total amount of compounds with n=2 or more is preferably 25 to 40 area%.

[0032]

Here, a method of producing the phenolic resin represented by Formula (2) will be described.

The method of producing the phenolic resin represented by Formula (2) is not particularly limited, and specifically, alkylphenols (3-methyl-6-t-butylphenol and 4-methyl-2-t-butylphenol) and p-hydroxybenzaldehyde are polycondensed under acidic conditions to form novolak. Alkylphenols (3-methyl-6-t-butylphenol and 4-methyl-2-t-butylphenol) and p-hydroxybenzaldehyde are preferably reacted at a ratio of 3:2 to 2:1. The ratio of 3-methyl-6-t-butylphenol and 4-methyl-2-t-butylphenol is preferably 90 wt% or more for 3-methyl-6-t-butylphenol in the alkylphenol, and this ratio is adjusted by the amount of the alkylphenol added when the phenolic resin is produced. Specifically, the alkylphenol as a raw material is prepared according to a desired introduction ratio of the alkylphenol.

The hydroxyl group equivalent of the obtained phenolic resin is preferably 140 to 170 g/eq., more preferably 145 to 165 g/eq., and particularly preferably 150 to 160 g/eq..

[0033]

Examples of acidic catalysts used when the phenolic resin represented by Formula (2) is synthesized include hydrochloric acid, sulfuric acid, sulfuric acid, formic acid, zinc chloride, ferric chloride, aluminum chloride, p-toluenesulfonic acid, methanesulfonic acid, activated clay, and ion-exchange resins. These may be used alone or two or more thereof may be used in combination. The amount of the catalyst used with respect to the phenolic hydroxyl group used is 0.1 to 50 wt% and preferably 1 to 30 wt%, and if the amount is too large, the amount of waste increases, and if the amount is too small, the progress of the reaction becomes slow down.

[0034]

The reaction may be performed using an organic solvent as necessary or performed without a solvent. However, since the reaction can proceed efficiently when water to be purified during the reaction is subjected to azeotropic dehydration, it is preferable to use a solvent that can azeotrope with water. In the present invention, it is particularly preferable to use a hydrocarbon-based organic solvent such as toluene or xylene.

Then, a process such as water washing or neutralization is performed, the resin can be taken out after the solvent is distilled off, or the resin can be taken out by a method such as reprecipitation or recrystallization. Since the phenolic resin represented by Formula (2) has a very high softening point, it is preferably taken out by a method such as reprecipitation or recrystallization, for example, a method such as precipitation by replacing a solvent with a poor solvent can be applied.

[0035]

The phenolic resin represented by Formula (2) is a crystal or a resin solid, and in that case, the amount for n=1 in GPC is preferably less than 60%. The amount is particularly 55 area% or less, and more preferably 50 area% or less. A total amount of residual raw material monomers is preferably 5 area% or less, and each peak is preferably less than 1.5 area%. The amount of this monomer affects the residual amount of the low-molecular-weight epoxy resin, and this amount affects heat resistance and the like.

[0036]

Next, the method of producing the epoxy resin of the present invention will be described.

As described above, the method of producing the epoxy resin of the present invention is not particularly limited, for example, it can be obtained by subjecting the

phenolic resin represented by Formula (2) and epihalohydrin to an addition or ring-closure reaction in the presence of a solvent and a catalyst.

The amount of epihalohydrin used with respect to 1 mol of the phenolic hydroxyl group of the phenolic resin is generally 1.0 to 20.0 mol, and preferably 1.5 to 10.0 mol.

[0037]

Examples of alkali metal hydroxides that can be used in the epoxidation reaction include sodium hydroxide and potassium hydroxide. The alkali metal hydroxide may be a solid or its aqueous solution may be used. When an aqueous solution is used, a method in which an aqueous solution of the alkali metal hydroxide is continuously added into a reaction system, water and epihalohydrin are distilled off under a reduced pressure or under atmospheric pressure continuously, water is additionally removed by liquid separation, and epihalohydrin continuously returns into the reaction system may be used. The amount of the alkali metal hydroxide used with respect to 1 mol of the phenolic hydroxyl group of the phenolic resin is generally 0.9 to 2.5 mol and preferably 0.95 to 1.5 mol. If the amount of the alkali metal hydroxide used is small, the reaction does not proceed sufficiently. On the other hand, an excessive amount of the alkali metal hydroxide used above 2.5 mol with respect to 1 mol of the phenolic hydroxyl group of the phenolic resin leads to unnecessary waste by-products.

[0038]

In order to promote the above reaction, a quaternary ammonium salt such as tetramethylammonium chloride, tetramethylammonium bromide, and trimethylbenzylammonium chloride may be added as a catalyst. The amount of the quaternary ammonium salt used with respect to 1 mol of the phenolic hydroxyl group of the phenolic resin is generally 0.1 to 15 g, and preferably 0.2 to 10 g. If the amount

used is too small, a sufficient reaction promoting effect is not obtained, and if the amount used is too large, the amount of quaternary ammonium salt remaining in the epoxy resin increases, which may cause deterioration in electrical reliability.

[0039]

During the epoxidation reaction, it is preferable to perform the reaction by adding alcohols such as methanol, ethanol, and isopropyl alcohol, or an aprotic polar solvent such as dimethyl sulfone, dimethyl sulfoxide, tetrahydrofuran, or dioxane in consideration of the reaction progress. When alcohols are used, the amount used is generally 2 to 50 wt% and preferably 4 to 20 wt% with respect to the amount of epihalohydrin used. In addition, when an aprotic polar solvent is used, its amount is generally 5 to 100 wt% and preferably 10 to 80 wt% with respect to the amount of epihalohydrin used. The reaction temperature is generally 30 to 90°C, and preferably 35 to 80°C. The reaction time is generally 0.5 to 100 hours and preferably 1 to 30 hours.

After the reaction is completed, the reaction product is heated under a reduced pressure with or without washing with water, and epihalohydrin, the solvent and the like are removed. In addition, in order to form an epoxy resin with a smaller hydrolyzable halogen content, the collected epoxy resin is dissolved in a solvent such as toluene or methyl isobutyl ketone, an aqueous solution of the alkali metal hydroxide such as sodium hydroxide or potassium hydroxide is added to proceed with the reaction, and ring closure can be secured. In this case, the amount of alkali metal hydroxide used with respect to 1 mol of the phenolic hydroxyl group of the phenolic resin used for glycidylation is generally 0.01 to 0.3 mol, and preferably 0.05 to 0.2 mol. The reaction temperature is generally 50 to 120°C, and the reaction time is generally 0.5 to 24 hours. After the reaction is completed, the salt produced is removed by filtration, washing with water or

the like, and the solvent is additionally distilled off by heating under a reduced pressure, and thus the epoxy resin of the present invention is obtained.

[0040]

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

Regarding the epoxy resin used in the curable resin composition of the present invention, the epoxy resin represented by Formula (1) may be used alone or may be used in combination with other epoxy resins. When used in combination, the proportion of the epoxy resin represented by Formula (1) in all epoxy resins is preferably 10 to 98 wt%, more preferably 30 to 95 wt%, and still more preferably 60 to 95 wt%. When the amount of the epoxy resin represented by Formula (1) added is 10% or more, it is possible to increase the elastic modulus and exhibit low water absorption.

[0041]

Specific examples of other epoxy resins that can be used in combination with the epoxy resin represented by Formula (1) include polycondensates of bisphenols (bisphenol A, bisphenol F, bisphenol S, biphenol, bisphenol AD, etc.) or phenols (phenol, alkyl-substituted phenol, aromatic-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted dihydroxybenzene, dihydroxynaphthalene, etc.) and various aldehydes (formaldehyde, acetaldehyde, alkylaldehyde, benzaldehyde, alkyl-substituted benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde, crotonaldehyde, cinnamaldehyde, etc.); polymers of the phenols and various diene compounds (dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, etc.); polycondensates of the phenols and ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone,

benzophenone, etc.); polycondensates of the phenols and aromatic dimethanols (benzenedimethanol, biphenyldimethanol, etc.); polycondensates of the phenols and aromatic dichloromethyls (α,α'-dichloroxylene, bischloromethylbiphenyl, etc.); polycondensates of the phenols and aromatic bisalkoxymethyls (bismethoxymethylbenzene, bismethoxymethylbiphenyl, bisphenoxymethylbiphenyl, etc.); and polycondensates of the bisphenols and various aldehydes, and glycidyl ether-based epoxy resins, alicyclic epoxy resins, glycidylamine-based epoxy resins, and glycidyl ester-based epoxy resins obtained by glycidylating alcohols and the like, and the present invention is not limited as long as they are epoxy resins that are generally used. These may be used alone or two or more thereof may be used.

[0042]

Examples of curing agents that can be used in the curable resin composition of the present invention include amine-based curing agents, acid anhydride-based curing agents, amide-based curing agents, and phenol-based curing agents. Specific examples of the curing agent that can be used include aromatic amine compounds such as o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, 2,2'-diaminodiphenylsulfone, diethyl toluene diamine, dimethylthio toluene diamine, diaminodiphenylmethane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 3,3'-diethyl-4,4'-diaminodiphenylmethane, 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetramethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetraisopropyldiphenylmethane, 4,4'-methylenebis(N-methylaniline), bis(aminophenyl)fluorene, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, bis[4-(4-aminophenoxy)phenyl]sulfone, 1,3'-bis(4-aminophenoxy)benzene, 1,4'-bis(4-

aminophenoxy)benzene, 1,4'-bis(4-aminophenoxy)biphenyl, 4,4'-(1,3-phenylenediisopropylidene)bisaniline, 4,4'-(1,4-phenylenediisopropylidene)bisaniline, naphthalenediamine, benzidine, dimethylbenzidine, and aromatic amine compound described in Synthesis Example 1 and Synthesis Example 2 in PCT International Publication No. WO2017/170551, and aliphatic amines such as 1,3-bis(aminomethyl)cyclohexane, isophoronediamine, 4,4'-methylenebis(cyclohexylamine), norbornanediamine, ethylenediamine, propanediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, dimerdiamine, and triethylenetetramine, but the present invention is not limited thereto, and the curing agent can be suitably used depending on properties desired to be imparted to the composition. It is preferable to use an aromatic amine in order to secure a pot lifespan, and it is preferable to use an aliphatic amine in order to impart quick curing. When an amine compound containing a bifunctional component as a main component is used as a curing agent, a highly linear network can be constructed during the curing reaction, and particularly, excellent toughness can be exhibited. In addition, examples thereof include amide compounds such as dicyandiamide, and a polyamide resin synthesized from a dimer of linolenic acid and ethylenediamine; acid anhydride-based compounds such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methylnadic anhydride, hexahydrophthalic anhydride, and methylhexahydrophthalic anhydride; phenolic compounds such as polycondensates of bisphenols (bisphenol A, bisphenol F, bisphenol S, biphenol, bisphenol AD, etc.) or phenols (phenol, alkyl-substituted phenol, aromatic-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted dihydroxybenzene, dihydroxynaphthalene, etc.) and various aldehydes (formaldehyde, acetaldehyde, alkylaldehyde, benzaldehyde, alkyl-substituted

benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde, crotonaldehyde, cinnamaldehyde, etc.), polymers of the phenols and various diene compounds (dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene, tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene, isoprene, etc.), polycondensates of the phenols and ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, etc.), polycondensates of the phenols and aromatic dimethanols (benzenedimethanol, biphenyldimethanol, etc.), polycondensates of the phenols and aromatic dichloromethyls (α,α'-dichloroxylene, bischloromethylbiphenyl, etc.), polycondensates of the phenols and aromatic bisalkoxymethyls (bismethoxymethylbenzene, bismethoxymethylbiphenyl, bisphenoxymethylbiphenyl, etc.), polycondensate of the bisphenols and various aldehydes, and modified products thereof; imidazole, trifluoroborane-amine complexes, and guanidine derivatives, but the present invention is not limited thereto.

[0043]

The amount of the curing agent used in the curable resin composition of the present invention with respect to 1 equivalent of the epoxy group of the epoxy resin is preferably 0.5 to 1.5 equivalent and particularly preferably 0.6 to 1.2 equivalent. If the amount is 0.5 to 1.5 equivalent, it is possible to obtain favorable cured object properties.

[0044]

When a curing reaction is performed using the curing agent, a curing accelerator may be used in combination. Examples of curing accelerators that can be used include imidazoles such as 2-methylimidazole, 2-ethylimidazole, 2-phenylimidazole, and 2-ethyl-4-methylimidazole, tertiary amines such as 2-(dimethylaminomethyl)phenol, triethylenediamine, triethanolamine, and 1,8-diazabicyclo(5,4,0)undecene-7, organic

phosphines such as triphenylphosphine, diphenylphosphine, and tributylphosphine, metal compounds such as tin octoate, tetra-substituted phosphonium·tetra-substituted borate such as tetraphenylphosphonium·tetraphenyl borate, and tetraphenylphosphonium·ethyl triphenyl borate, tetraphenyl boron salts such as 2-ethyl-4-methylimidazole·tetraphenyl borate, and N-methylmorpholine·tetraphenyl borate, and carboxylic acid compounds such as benzoic acid, phthalic acid, isophthalic acid, telephthalic acid, naphthoic acid, and salicylic acid. In order to promote a curing reaction between the amine compound and the epoxy resin, a carboxylic acid compound such as salicylic acid is preferable. 0.01 to 15 parts by weight of the curing accelerator with respect to 100 parts by weight of the epoxy resin is used as necessary.

[0045]

In addition, an inorganic filler can be added to the curable resin composition of the present invention as necessary. Examples of inorganic fillers include powders of crystalline silica, fused silica, alumina, zircon, calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, forsterite, steatite, spinel, titania, talc and the like and beads made by spheroidizing these powders, and the present invention is not limited thereto. These may be used alone or two or more thereof may be used. The amount of these inorganic fillers used varies depending on applications, and for example, when fillers are used as the encapsulant for semiconductors, in terms of the heat resistance, moisture resistance, mechanical properties, flame retardancy and the like of the cured object of the curable resin composition, the proportion of the fillers used in the curable resin composition is preferably 20 wt% or more, more preferably 30 wt% or more, and particularly preferably 70 to 95 wt% in order to increase the linear expansion coefficient with a lead frame.

Here, in the present invention, the content of inorganic fillers is important to improve particularly tracking resistance performance. In consideration of tracking resistance performance, the content of the inorganic filler in the total amount of the curable resin composition of the present invention is preferably 74 wt% or more and 95 wt% or less, and particularly preferably 78 wt% or more and 95 wt% or less. It has been confirmed that, in the case of the epoxy resin of the present invention structure, if the content is 74 wt% or more, the tracking resistance performance is greatly improved, and if the content is less than 74 wt%, for example, if the content is less than 70 wt%, the tracking performance is less superior to other epoxy resins.

[0046]

A release agent can be added to the curable resin composition of the present invention in order to facilitate release from a mold during molding. As the release agent, any of conventionally known agents can be used, and examples thereof include ester waxes such as carnauba wax and montan wax, fatty acids such as stearic acid and palmitic acid, and metal salts thereof, and polyolefin waxes such as oxidized polyethylene and non-oxidized polyethylene. These may be used alone or two or more thereof may be used in combination. The amount of these release agents added with respect to the total organic component is preferably 0.5 to 3 wt%. If the amount is too small, release from the mold becomes poor, and if the amount is too large, adhesion to the lead frame or the like becomes poor.

[0047]

A coupling agent can be added to the curable resin composition of the present invention in order to improve adhesion between the inorganic filler and the resin component. As the coupling agent, any of conventionally known agents can be used, and examples thereof include various alkoxysilane compounds such as

vinylalkoxysilanes, epoxyalkoxysilanes, styrylalkoxysilanes, methacryloxyalkoxysilanes, acryloxyalkoxysilanes, aminoalkoxysilanes, mercaptoalkoxysilanes, and isocyanatoalkoxysilanes, alkoxy titanium compounds, and aluminum chelates. These may be used alone or two or more thereof may be used in combination. As the method of adding a coupling agent, the surface of the inorganic filler may be treated with a coupling agent in advance and then kneaded with the resin, or the resin may be mixed with the coupling agent and then kneaded with the inorganic filler.

[0048]

In addition, the curable resin composition of the present invention may contain known additives as necessary. Specific examples of additives that can be used include polybutadiene and their modified products, modified products of acrylonitrile copolymers, polyphenylene ether, polystyrene, polyethylene, polyimide, fluorine resins, maleimide compounds, cyanate ester compounds, silicone gel, silicone oil, and coloring agents such as carbon black, phthalocyanine blue, and phthalocyanine green.

[0049]

The curable resin composition of the present invention is obtained by uniformly mixing the above components. The curable resin composition of the present invention can be easily cured by the same method as the conventionally known method. For example, an epoxy resin, a curing agent, and as necessary, a curing accelerator, an inorganic filler, a release agent, a silane coupling agent and an additive are sufficiently mixed using an extruder, a kneader, a roller or the like as necessary, until the mixture becomes uniform and thereby a curable resin composition of the present invention is obtained, this composition is molded using a melt casting method, a transfer molding method, an injection molding method, a compression molding method or the like, and additionally heated at 80 to 200°C for 2 to 10 hours and thereby a cured object can be

obtained.

[0050]

In addition, the curable resin composition of the present invention may contain a solvent as necessary. A curable resin composition containing a solvent (epoxy resin varnish) can be made into a cured object of the curable resin composition of the present invention by hot-press molding a prepreg obtained by impregnating a fibrous material (base material) such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, alumina fibers, and paper and heating and drying it. The content (wt%) of the solvent in the curable resin composition is generally 10 to 70 wt%, and preferably about 15 to 70 wt%. Examples of solvents include amide solvents such as γ-butyrolactones, N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylimidazolidinone; sulfones such as tetramethylene sulfone; ether solvents such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether monoacetate, and propylene glycol monobutyl ether, and preferably mono- or di-lower (C1-3) alkyl ethers of lower (C1-3) alkylene glycol; and ketone solvents such as methyl ethyl ketone and methyl isobutyl ketone, and more preferably, examples thereof include di-lower (C1-3) alkyl ketone in which two alkyl groups may be the same as or different from each other; and aromatic solvents such as toluene and xylene. These may be used alone or a mixed solvent of two or more thereof may be used.

[0051]

In addition, a sheet-like adhesive can be obtained by applying the epoxy resin varnish onto a release film, removing the solvent under heating, and performing B stage. This sheet-like adhesive can be used as an interlayer insulating layer in a multi-layer substrate or the like.

[0052]

The cured object obtained in the present invention can be used for various applications. Specifically, general applications in which a thermosetting resin such as an epoxy resin is used may be exemplified, and for example, in addition to adhesives, paints, coating agents, molding materials (including sheets, films, FRP, etc.), insulating materials (including print substrates, wire coatings, etc.), and encapsulants, additives for other resins and the like may be exemplified.

[0053]

Examples of adhesives include adhesives for civil engineering, adhesives for construction, adhesives for automobiles, adhesives for general office, and adhesives for medical care, as well as adhesives for electronic materials. Among these, adhesives for electronic materials include, for example, interlayer adhesives for multi-layer substrates such as build-up substrates, adhesives for semiconductors such as die bonding agents and underfills, and adhesives for mounting such as underfills for BGA reinforcement, anisotropic conductive films (ACF), and anisotropic conductive pastes (ACP).

[0054]

Examples of encapsulants include potting, dipping, and transfer mold encapsulants for capacitors, transistors, diodes, light emitting diodes, ICs, and LSIs, potting encapsulants for COB, COF, TAB and the like of ICs and LSIs, and encapsulants (including underfills for reinforcement) when IC packages such as underfills for flip chips, QFP, BGA, and CSP are mounted.

[Examples]

[0055]

Next, the present invention will be described in more detail with reference to examples, and in the following, unless otherwise specified, the parts are parts by weight.

However, the present invention is not limited to these examples.

[0056]

·epoxy equivalent

measured by the method according to JIS K-7236.

·softening point

measured using a softening point measuring instrument FP90 (commercially available from METTLER TOLEDO).

·hydroxyl group equivalent

A sample was subjected to acetylation in a pyridine solution with acetic anhydride and an acid anhydride remaining in water after acetylation was completed was decomposed. This was titrated with a 0.5 N KOH ethanol solution using a potentiometric titrator to measure the amount of free acetic acid, and the hydroxyl group equivalent was determined from the results.

[0057]

·GPC (gel permeation chromatography)

(Measurement condition 1)

device: Waters e2695

column: a total of four columns of SHODEX GPC KF-401HQ, KF-402HQ, KF-403HQ, and KF-404HQ

flow rate: 0.3 ml/min

column temperature: 40°C

solvent used: THF (tetrahydrofuran)

detector: UV 254 nm

(Measurement condition 2)

device: HLC-8220GPC (commercially available from Tosoh Corporation)

column: a total of 3 columns of 1 column of TSK gel G3000HXL and 2 columns of TSK gel G2000HXL (commercially available from Tosoh Corporation)

flow rate: 1.065 ml/min

column temperature: 40°C

solvent used: THF (tetrahydrofuran)

detector: UV 254 nm

(Measurement condition 3)

device: HLC-8420GPC (commercially available from Tosoh Corporation)

column: a total of 3 columns of 1 column of TSK gel G3000HXL and 2 columns of TSK gel G2000HXL (commercially available from Tosoh Corporation)

flow rate: 1.065 ml/min

column temperature: 40°C

solvent used: THF (tetrahydrofuran)

detector: UV 254 nm

standard polystyrene (commercially available from Tosoh Corporation)

PStQuickC, PStQuickD (corrected by adding styrene as an internal standard when the molecular weight was measured)

[0058]

[Synthesis Example 1]

137.2 parts of 3-methyl-6-t-butylphenol, 0.16 parts of 4-methyl-2-t-butylphenol, 60 parts of p-hydroxybenzaldehyde, 142 parts of toluene, and 1.4 parts of p-toluenesulfonic acid were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the reaction was caused at 110 to 115°C for 8 hours. After the reaction was completed, 25% NaOH water was

added and toluene was then distilled off by azeotropic dehydration. Then, 75% sulfuric acid was added, the pH was adjusted to 5 to 7, the precipitated resin powder was filtered and dried at 60°C to obtain 186 parts of a phenolic resin (P1). The obtained phenolic resin (P1) was in the form of powder, the softening point was 150°C or higher, the hydroxyl group equivalent was 155 g/eq., and 48.8 area% was for n=1 according to GPC. GPC charts (measurement condition 1) are shown in Fig. 1.

[0059]

[Synthesis Example 2]

153.1 parts of 3-methyl-6-t-butylphenol, 0.17 parts of 4-methyl-2-t-butylphenol, 60 parts of p-hydroxybenzaldehyde, 142 parts of toluene, and 0.6 parts of p-toluenesulfonic acid were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the reaction was caused at 100 to 105°C for 6 hours. After the reaction was completed, 25% NaOH water was added and toluene was then distilled off by azeotropic dehydration. Then, 75% sulfuric acid was added, the pH was adjusted to 5 to 7, the precipitated resin powder was filtered and dried at 60°C to obtain 198 parts of a phenolic resin (P2). The obtained phenolic resin (P2) was in the form of powder, the softening point was 150°C or higher, the hydroxyl group equivalent was 144 g/eq., and 51.7 area% was for n=1 according to GPC. GPC charts (measurement condition 1) are shown in Fig. 2.

[0060]

[Synthesis Example 3]

137.2 parts of 3-methyl-6-t-butylphenol, 0.16 parts of 4-methyl-2-t-butylphenol, 60 parts of p-hydroxybenzaldehyde, 142 parts of toluene, and 1.4 parts of p-toluenesulfonic acid were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the reaction was caused

at 110 to 115°C for 8 hours. After the reaction was completed, 25% NaOH water was added and toluene was then distilled off by azeotropic dehydration. Then, 75% sulfuric acid was added, the pH was adjusted to 5 to 7, the precipitated resin powder was filtered and dried at 60°C to obtain 180 parts of a phenolic resin (P3). The obtained phenolic resin (P3) was in the form of powder, the softening point was 150°C or higher, the hydroxyl group equivalent was 153 g/eq., and 47.6 area% was for n=1 according to GPC. GPC charts (measurement condition 1) are shown in Fig. 3.

[0061]

[Example 1]

310 parts of the phenolic resin (P1) obtained in Synthesis Example 1, 973 parts of epichlorohydrin, 274 parts of dimethyl sulfoxide, and 15 parts of water were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the internal temperature was raised to 45°C. After 16 parts of sodium hydroxide was added in a divided manner over 1.5 hours, the reaction was caused at 45°C for 2 hours and at 70°C for 1 hour. The unreacted epichlorohydrin and solvent were distilled off by heating under a reduced pressure. 1,040 parts of MIBK was added, and the organic layer was washed once with 440 parts of water. The organic layer was returned to the reaction container, 20 parts of a 30 wt% aqueous sodium hydroxide solution was added, and the mixture was reacted at 70°C for 2 hours. After being cooled, the organic layer was washed four times with 130 parts of water, the solvent was distilled off by heating under a reduced pressure, and 170 parts of an epoxy resin (E1) as a solid resin was obtained. The epoxy equivalent was 214 g/eq., the ICI viscosity (150°C) was 0.57 Pa·s, the softening point was 100°C, and the parameter A was 2.14. The average repeating unit n calculated by GPC (detector UV 254 nm) was 2.4, 42.3 area% was for n=1, and 1.57 area% was for n=less than 1. GPC charts

(measurement condition 2) are shown in Fig. 4.

[0062]

[Example 2]

310 parts of the phenolic resin (P1) obtained in Synthesis Example 1, 584 parts of epichlorohydrin, 274 parts of dimethyl sulfoxide, and 15 parts of water were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the internal temperature was raised to 45°C. After 16 parts of sodium hydroxide was added in a divided manner over 1.5 hours, the reaction was caused at 45°C for 2 hours and at 70°C for 1 hour. The unreacted epichlorohydrin and solvent were distilled off by heating under a reduced pressure. 1,040 parts of MIBK was added, and the organic layer was washed once with 440 parts of water. The organic layer was returned to the reaction container, 20 parts of a 30 wt% aqueous sodium hydroxide solution was added, and the reaction was caused at 70°C for 2 hours. After being cooled, the organic layer was washed four times with 130 parts of water, the solvent was distilled off by heating under a reduced pressure, and 141 parts of an epoxy resin (E2) as a solid resin was obtained. The epoxy equivalent was 225 g/eq., the ICI viscosity (150°C) was 1.92 Pa·s, the softening point was 110°C, and the parameter A was 2.05. The average repeating unit n calculated by GPC (detector UV 254 nm) was 2.9, 31.1 area% was for n=1, and 1.28 area% was for n=less than 1. GPC charts (measurement condition 2) are shown in Fig. 5.

[0063]

[Example 3]

310 parts of the phenolic resin (P3) obtained in Synthesis Example 3, 778 parts of epichlorohydrin, 274 parts of dimethyl sulfoxide, and 15 parts of water were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while

purging with nitrogen, and the internal temperature was raised to 45°C. After 16 parts of sodium hydroxide was added in a divided manner over 1.5 hours, the reaction was caused at 45°C for 2 hours and at 70°C for 1 hour. The unreacted epichlorohydrin and solvent were distilled off by heating under a reduced pressure. 1,040 parts of MIBK was added, and the organic layer was washed once with 440 parts of water. The organic layer was returned to the reaction container, 20 parts of a 30 wt% aqueous sodium hydroxide solution was added, and the mixture was reacted at 70°C for 2 hours. After being cooled, the organic layer was washed four times with 130 parts of water, the solvent was distilled off by heating under a reduced pressure, and 303 parts of an epoxy resin (E3) as a solid resin was obtained. The epoxy equivalent was 216 g/eq., the total chlorine concentration was 440 ppm (according to ISO21627-3), the inorganic chloride ion concentration was 0.3 ppm, the ICI viscosity (150°C) was 0.64 Pa·s, the softening point was 100°C, and the parameter A was 2.16. Mn calculated by GPC (detector UV 254 nm) was 1,059, Mw was 2001 (in terms of polystyrene), 39.5 area% was for n=1, and 1.95 area% was for n=less than 1. GPC charts (measurement condition 3) are shown in Fig. 6.

[0064]

[Comparative Synthesis Example 1]

288 parts of the phenolic resin (P2) obtained in Synthesis Example 2, 584 parts of epichlorohydrin, 274 parts of dimethyl sulfoxide, and 15 parts of water were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the internal temperature was raised to 45°C. After 16 parts of sodium hydroxide was added in a divided manner over 1.5 hours, the reaction was caused at 45°C for 2 hours and at 70°C for 1 hour. The unreacted epichlorohydrin and solvent were distilled off by heating under a reduced pressure. 1,040 parts of MIBK

was added, and the organic layer was washed once with 440 parts of water. The organic layer was returned to the reaction container, 20 parts of a 30 wt% aqueous sodium hydroxide solution was added, and the mixture was reacted at 70°C for 2 hours. After being cooled, the organic layer was washed four times with 130 parts of water, the solvent was distilled off by heating under a reduced pressure, and 165 parts of an epoxy resin (E4) as a solid resin was obtained. The epoxy equivalent was 223 g/eq., the ICI viscosity (150°C) was 0.60 Pa·s, the softening point was 99.7°C, and the parameter A was 2.24. The average repeating unit n calculated by GPC was 2.4, 43.9 area% was for n=1, and 1.9 area% was for n=less than 1. GPC charts (measurement condition 2) are shown in Fig. 7.

[0065]

[Comparative Synthesis Example 2]

288 parts of the phenolic resin (P2) obtained in Synthesis Example 2, 487 parts of epichlorohydrin, 274 parts of dimethyl sulfoxide, and 15 parts of water were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the internal temperature was raised to 45°C. After 16 parts of sodium hydroxide was added in a divided manner over 1.5 hours, the reaction was caused at 45°C for 2 hours and at 70°C for 1 hour. The unreacted epichlorohydrin and solvent were distilled off by heating under a reduced pressure. 1,040 parts of MIBK was added, and the organic layer was washed once with 440 parts of water. The organic layer was returned to the reaction container, 20 parts of a 30 wt% aqueous sodium hydroxide solution was added, and the mixture was reacted at 70°C for 2 hours. After being cooled, the organic layer was washed four times with 130 parts of water, the solvent was distilled off by heating under a reduced pressure, and 161 parts of an epoxy resin (E5) as a solid resin was obtained. The epoxy equivalent was 224 g/eq., the ICI

viscosity (150°C) was 0.66 Pa·s, the softening point was 100.9°C, and the parameter A was 2.22. The average repeating unit n calculated by GPC was 2.3, 43 area% was for n=1, and 2.1 area% was for n=less than 1. GPC charts (measurement condition 2) are shown in Fig. 8.

[0066]

[Examples 4 and 5 and Comparative Examples 1 and 2]

Using the epoxy resins E1, E2, and E4 obtained in examples and synthesis examples, and FAE-2500 (commercially available from Nippon Kayaku Co., Ltd., analysis results will be described below) as E6, a trisphenolmethane type phenolic resin (KAYAHARD KTG-105 commercially available from Nippon Kayaku Co., Ltd.) as a curing agent, and triphenylphosphine as a catalyst, an equivalent amount of the trisphenolmethane type phenolic resin to the epoxy resin, and 1 phr. of triphenylphosphine to the epoxy resin were added, and mixed and kneaded using a mixing roll until the mixture became uniform, and additionally, after demolding, curing was performed under conditions at 160°C for 2 hours and at 180°C for 6 hours to obtain an evaluation test piece.

[0067]

The epoxy equivalent of FAE-2500 was 213 g/eq., the ICI viscosity (150°C) was 0.30 Pa·s, the softening point was 93.5°C, and the parameter A was 2.28. GPC charts (measurement condition 2) are shown in Fig. 9.

[0068]

The evaluation test piece was measured under the following conditions, and the results are shown in Table 1. In addition, TMA charts are shown in Fig. 10.

[0069]

<Dynamic viscoelasticity measurement (DMA)>

The glass transition temperature (temperature at which tanδ reaches the maximum value), and the value of tanδ at that time were measured using a dynamic viscoelasticity tester.

·dynamic viscoelasticity measuring instrument: commercially available from TA-instrumentsDMA-2980

·temperature rise rate: 2°C/min

[0070]

<Thermomechanical property measurement (TMA)>

The glass transition temperature (Tg) and the coefficient of thermal expansion (CTE) were evaluated using a thermomechanical property measurement device.

[0071]

<Thermogravimetric-differential thermal analysis (TG-DTA)>

The thermal decomposition temperature and the residual carbon content at 500°C were measured using TG-DTA.

measurement sample: 5 to 10 mg of powder (passed through 100 μm mesh, on 75 μm mesh) used

measurement conditions: temperature rise rate of 10°C/min Air flow 200 ml

[0072]

[Table 1]

		Example 4	Example 5	Comparative Example 1	Comparative Example 2
Epoxy resin used	Sample name	E1	E2	E4	E6
	Parameter A	2.14	2.05	2.24	2.28
DMA	Tg (°C)	241	252	233	232
	Tanδ	0.63	0.45	0.74	0.76
TMA	Tg (°C)	234	240	222	218
CTE	α1	78	78	81	86
	α2	198	194	207	209

TG-DTA	5% weight reduction (°C)	304	304	305	303
	Residual carbon at 500°C	18%	18%	18%	16%

[0073]

[Example 6 and Comparative Example 3]

The epoxy resin (E1), the epoxy resin (E6, FAE-2500 (commercially available from Nippon Kayaku Co., Ltd.)), a xyloc type phenolic resin (MEHC-7800SS commercially available from Meiwa Plastic Industries, Ltd.) as a curing agent, triphenylphosphine (TPP, commercially available from Tokyo Chemical Industry Co., Ltd.) as a catalyst, silica gel (fused silica MSR-2212, commercially available from Tatsumori Ltd.) as an inorganic filler, carnauba wax (commercially available from Cerarica Noda Co., Ltd.) as a release agent, and a silane coupling agent (product name: KBM-303 commercially available from Shin-Etsu Chemical Co., Ltd.) as an additive were used, and these were uniformly mixed and kneaded using a mixing roll to obtain a curable resin composition.

This curable resin composition was pulverized and then formed into a tablet using a tablet machine. The tableted curable resin composition was subjected to transfer molding (at 175°C for 60 to 150 minutes), and after demolding, curing was performed under conditions of 160°C×2 hours+180°C×6 hours to obtain an evaluation test piece. The following evaluation was performed using this test piece. The measurement results are shown in Table 2.

[0074]

<Tracking resistance test>

applicable standards: IEC-Pub. 60112-2003 (4th edition) and JIS-C2134-2007

target test voltage: 400 V to 600 V

test solution: ammonium chloride 0.1% aqueous solution

the number of drops: 50 drops, if the test piece was broken with less than 50 drops, it was determined as NG.

temperature and humidity in test room: 21°C to 23°C, 40 to 45% RH

test device: YST-112 type tracking resistance tester (commercially available from Yamayoshi Kenki. COM)

shape of test sample: diameter 50 mm, thickness 3 mm

1 point measurement per sheet

[0075]

[Table 2]

		Example 6	Comparative Example 3
Formulation	Epoxy resin E1	10.7	
	Epoxy resin E6		10.7
	MEHC-7800SS	8.5	
	TPP	0.2	0.2
	MSR-2212	85	85
	Carnauba wax	0.3	0.3
	KBM-303	0.3	0.3
Number of drops until breakage	500 V (n=1)	>50	>50
	600 V (n=3)	>50	>50

[0076]

Based on the results of Table 1, it was confirmed that the epoxy resin of the present invention had high heat resistance and dimensional stability (low linear expansion). In addition, based on the results of Table 2, it was confirmed that the epoxy resin of the present invention had high tracking resistance performance.

[0077]

[Synthesis Example 4]

130.3 parts of 3-methyl-6-t-butylphenol, 0.2 parts of 4-methyl-2-t-butylphenol, 60 parts of p-hydroxybenzaldehyde, 142 parts of toluene, and 1.4 parts of p-

toluenesulfonic acid were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the reaction was caused at 110 to 115°C for 8 hours. After the reaction was completed, 25% NaOH water was added and toluene was then distilled off by azeotropic dehydration. Then, 75% sulfuric acid was added, the pH was adjusted to 5 to 7, the precipitated resin powder was filtered and dried at 60°C to obtain 186 parts of a phenolic resin (P4). The obtained phenolic resin (P4) was in the form of powder, the softening point was 200°C or higher, the hydroxyl group equivalent was 160 g/eq., and 37.0 area% was for n=1 according to GPC. GPC charts (measurement condition 1) are shown in Fig. 11.

[0078]

[Example 7]

320 parts of the phenolic resin (P4) obtained in Synthesis Example 4, 973 parts of epichlorohydrin, 274 parts of dimethyl sulfoxide, and 15 parts of water were put into a flask including a thermometer, a cooling pipe, a fractionating pipe, and a stirrer while purging with nitrogen, and the internal temperature was raised to 45°C. After 16 parts of sodium hydroxide was added in a divided manner over 1.5 hours, the reaction was caused at 45°C for 2 hours and at 70°C for 1 hour. The unreacted epichlorohydrin and solvent were distilled off by heating under a reduced pressure. 1,040 parts of MIBK was added, and the organic layer was washed once with 440 parts of water. The organic layer was returned to the reaction container, 20 parts of a 30 wt% aqueous sodium hydroxide solution was added, and the mixture was reacted at 70°C for 2 hours. After being cooled, the organic layer was washed four times with 130 parts of water, the solvent was distilled off by heating under a reduced pressure, and 107 parts of an epoxy resin (E7) as a solid resin was obtained. The epoxy equivalent was 220 g/eq., the ICI viscosity (150°C) was 0.8 Pa·s or more, the softening point was 108.5°C, and the

parameter A was 2.03. The average repeating unit n calculated by GPC (detector UV 254 nm) was 3.4, 24.9 area% was for n=1, and 2.91 area% was for n=less than 1. GPC charts (measurement condition 3) are shown in Fig. 12. In addition, each peak was 1.75area% with a retention time of 35.619 minutes, and the other peaks were 1.5 area% or less.

[0079]

[Examples 8 and 9]

The epoxy resins E3 and E7 obtained in the above examples, trisphenolmethane type phenolic resin (KAYAHARD KTG-105 commercially available from Nippon Kayaku Co., Ltd., a hydroxyl group equivalent of 102 g/eq.) as a curing agent, biphenyl aralkyl type phenolic resin (KAYAHARD GPH-65 commercially available from Nippon Kayaku Co., Ltd., curing agent a hydroxyl group equivalent of 200 g/eq.), triphenylphosphine (TPP, commercially available from Tokyo Chemical Industry Co., Ltd.) as a catalyst, silica gel (fused silica MSR-2212, commercially available from Tatsumori Ltd.) as an inorganic filler, carnauba wax (commercially available from Cerarica Noda Co., Ltd.) as a release agent, and a silane coupling agent (product name: KBM-303 commercially available from Shin-Etsu Chemical Co., Ltd.) as an additive were used, and mixed at the ratio (parts by weight) shown in Table 3, and uniformly mixed and kneaded using a mixing roll, and additionally, after demolding, curing was performed under conditions at 160°C for 2 hours and at 180°C for 6 hours to obtain an evaluation test piece. The tracking resistance test was performed using this test piece. The measurement results are shown in Table 3.

[0080]

[Table 3]

		Example 8	Example 9

Formulation	Epoxy resin E3		22
	Epoxy resin E7	22	
	KTG-105	10	
	GPH-65		20
	TPP	0.4	0.4
	MSR-2212	180	238
	Carnauba wax	0.5	0.7
	KBM-303	0.5	0.7
Number of drops until breakage	500 V (n=1)	>50	>50
	600 V (n=3)	>50	>50

[0081]

[Example 9 and Comparative Example 4]

The epoxy resin E1 obtained in the above example and a biphenyl aralkyl type epoxy resin (NC-3000 commercially available from Nippon Kayaku Co., Ltd.), a xyloc type phenolic resin (MEHC-7800SS commercially available from Meiwa Plastic Industries, Ltd.) as a curing agent, triphenylphosphine (TPP, commercially available from Tokyo Chemical Industry Co., Ltd.) as a catalyst, silica gel (fused silica MSR-2212, commercially available from Tatsumori Ltd.) as an inorganic filler, carnauba wax (commercially available from Cerarica Noda Co., Ltd.) as a release agent, and a silane coupling agent (product name: KBM-303 commercially available from Shin-Etsu Chemical Co., Ltd.) as an additive were used, and uniformly mixed and kneaded using a mixing roll to obtain a curable resin composition.

This curable resin composition was pulverized and then formed into a tablet using a tablet machine. The tableted curable resin composition was subjected to transfer molding (at 175°C for 60 to 15 minutes), and additionally, after demolding, curing was performed under conditions of 160°C×2 hours+180°C×6 hours to obtain an evaluation test piece. The tracking resistance test was performed using this test piece. The measurement results are shown in Table 4.

[0082]

[Table 4]

		Example 9	Comparative Example 4
Formulation	Epoxy resin E1	21.4	
	NC-3000		27.4
	MEHC-7800SS (equivalent amount)	17	17
	TPP	0.4	0.4
	MSR-2212	187	217
	Carnauba wax	0.562	0.650
	KBM-303	0.562	0.650
Number of drops until breakage	500 V (n=1)	>50	>50
	600 V (n=3)	>50	NG

[0083]

[Examples 10 to 13 and Comparative Examples 5 to 8]

The epoxy resin E1 obtained in the above example and a biphenyl aralkyl type epoxy resin (NC-3000 commercially available from Nippon Kayaku Co., Ltd.), a xyloc type phenolic resin (MEHC-7800SS commercially available from Meiwa Plastic Industries, Ltd.) as a curing agent, a biphenyl aralkyl type phenolic resin (KAYAHARD GPH-65 commercially available from Nippon Kayaku Co., Ltd.), triphenylphosphine (TPP, commercially available from Tokyo Chemical Industry Co., Ltd.) as a catalyst, silica gel (fused silica MSR-2212, commercially available from Tatsumori Ltd.) as an inorganic filler, carnauba wax (commercially available from Cerarica Noda Co., Ltd.) as a release agent, and a silane coupling agent (product name: KBM-303 commercially available from Shin-Etsu Chemical Co., Ltd.) as an additive were used and uniformly mixed kneaded using a mixing roll to obtain a curable resin composition.

This curable resin composition was pulverized and then formed into a tablet using a tablet machine. The tableted curable resin composition was subjected to transfer molding (at 175°C for 60 to 15 minutes), and additionally, after demolding, curing was performed under conditions of 160°C×2 hours+180°C×6 hours to obtain an

evaluation test piece. The tracking resistance test was performed using this test piece. Particularly, the CTI was measured using a measurement method according to IEC-Pub. 60112-2003 (4th edition). The measurement results are shown in Table 5 and Fig. 13.

[0084]

[Table 5]

		Example 10	Example 11	Example 12	Example 13	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Formulation	Epoxy resin E1	21.4	21.4	21.4	21.4				
	NC-3000					27.4	27.4	27.4	27.4
	GPH-65 (equivalent amount)	20	20	20	20	20	20	20	20
	TPP	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	MSR-2212	202	166	124	97	231	190	142	111
	Carnauba wax	0.606	0.497	0.373	0.290	0.694	0.569	0.427	0.332
	KBM-303	0.606	0.497	0.373	0.290	0.694	0.569	0.427	0.332
	Content of inorganic fillers in total amount of curable resin composition (wt%)	82	79	74	70	82	79	75	70
Test result	CTI	600	400	250	175	450	225	225	175
	PLC	1	2	3	4	2	3	3	4

[0085]

Based on the above results, it was confirmed that the cured object using the epoxy resin of the present invention maintained a relatively high CTI, and particularly, when the amount of the inorganic filler added was 74 wt% or more and more preferably 78 wt% or more, the rate of increase in CTI was higher than that of other compositions.

[Industrial Applicability]

[0086]

The epoxy resin of the present invention is beneficial for applications to automotive materials, particularly, power device peripheral materials, and particularly applications for which heat resistance and a high comparative tracking index (CTI) are required.