

5 PHOSPHORUS-CONTAINING EPOXY RESIN

Field of the Disclosure

The present disclosure relates generally to epoxy resins and in particular halogen-free, phosphorus-containing epoxy resins.

Background

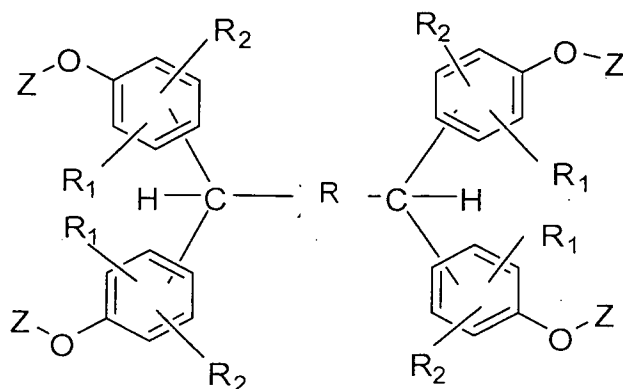
10 Epoxy resins are used in both industrial and consumer electronics because of, among other things, their chemical resistance, mechanical strength and electrical properties. For example, epoxy resins can be used in electronics as laminates, adhesive materials and/or insulating materials, such as interlayer insulating films. To be useful for these applications, the epoxy resins need to provide certain necessary
15 physical, thermal, electrical insulation and moisture resistance properties. For example, it is advantageous for epoxy resins used for electric applications to have a high glass transition temperature (T_g).

Epoxy resins, however, can be flammable. As such, different approaches have been made to impart flame resistance to epoxy resins. Two main approaches have
20 been taken to provide flame resistance. The first approach makes use of halogen compounds. Halogen-containing compounds have been commonly used in the electronic industry to impart flame resistance to electrical and electronic assemblies. For example, tetrabromobisphenol-A (TBBA) is a typical halogen-containing compound that has been widely used as a flame retardant for epoxy resins. Although
25 halogen-containing compounds can be effective, they are considered by some to be undesirable from an environmental standpoint due to the possibility of formation hazardous substances during the incineration of electronic components at their end of life. The second approach, in a response to the environmental concerns of the first approach, is an “environmentally friendly” approach in which halogen-free
30 compounds are used to impart flame retardancy.

Summary

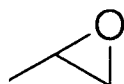
Embodiments of the present disclosure include a phosphorus-containing epoxy resin of a compound of Formula (I):

5 (Formula I)



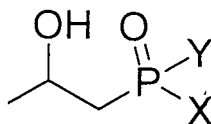
wherein each Z is independently a compound of Formula (II):

10 (Formula II)



, a compound of Formula (III):

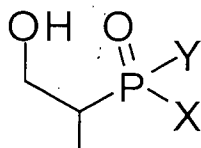
(Formula III)



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, or a compound of Formula (IV):

(Formula IV)



wherein:

20 each R₁ and R₂ is independently hydrogen or an alkyl moiety;

R in the compound of Formula (I) is a cycloaliphatic diradical, a bicyclic aliphatic diradical, or a tricyclic aliphatic diradical having 6 to 30 carbons; and

wherein each Y and X is independently hydrogen, an aliphatic moiety having 1 to 20 carbon atoms or an aromatic hydrocarbon moiety having 6 to 20 carbon atoms.

5 Embodiments of the present disclosure also include a curable composition formed with the phosphorus-containing epoxy resin. For the various embodiments, the curable compositions can include a phosphorus-content of within a range of from 1 weight percent (wt%) to 4 wt%.

10 Embodiments of the present disclosure also include a cured epoxy that is formed with the phosphorus-containing epoxy resin. For the various embodiments, the cured epoxy can have a glass transition temperature (T_g) of within a range of 150 degrees Celsius (°C) to 200 °C.

15 Embodiments of the present disclosure further include a process for making the phosphorus-containing epoxy resin that includes providing an epoxy resin with a functionality of at least 3 by epoxidizing a reaction product of a condensation of phenol and a dialdehyde, and reacting the epoxy resin with a phosphorus compound that contains a phosphorus-hydrogen moiety.

Detailed Description

20 Embodiments of the present disclosure include a phosphorus-containing epoxy resin that can be used as, among other things, a self-curing compound and/or as a component in a curable composition to form a cured epoxy. The phosphorus-containing epoxy resin of the present disclosure can also be used with other epoxy resins in curable compositions to increase the thermal resistance (*e.g.*, T_d and T_g discussed herein) of the cured epoxies formed with the other epoxy resins.

25 The phosphorus-containing epoxy resin of the present disclosure also provides the advantage of being halogen free while acting as a flame retardant for a cured epoxy formed in part with the phosphorus-containing epoxy resin. Such cured epoxies formed with the phosphorus-containing epoxy resin can also have suitable thermal and electrical properties useful for electronic applications including electrical laminates, interconnect substrates, build-up films, solder masks, castings, and adhesives.

30 Specifically, the phosphorus-containing epoxy resin of the present disclosure can provide improvements in thermomechanical properties, such as increasing the glass transition temperature of the cured epoxy.

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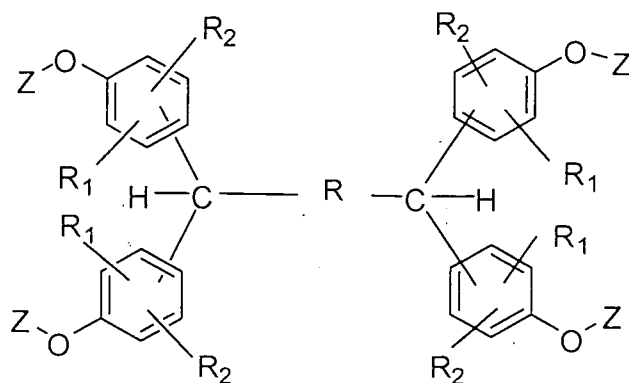
5 The improvements of the present disclosure can include increasing the glass transition temperature (T_g) of cured epoxies formed with the phosphorus-containing epoxy resin such that the phosphorus-containing epoxy resin can be used for mid-to-high range applications that undergo temperatures of at least 150 °C, and preferably temperatures of at least 170 °C. In addition, curable compositions formed with the phosphorus-containing epoxy resin of the present disclosure may also provide, in addition to flame resistance, other desired physical properties, such as thermal resistance. One method for measuring thermal resistance is to measure the thermal decomposition temperature (T_d) by determining the temperature at which 5 weight percent (wt%) of a cured epoxy degrades as a sample is heated at a fixed rate.

10 Phosphorus-containing epoxy resins of the present disclosure can provide cured epoxy resins with T_d 's of at least 330 °C.

Additionally, the phosphorus-containing epoxy resins of the present disclosure can have a molar ratio of epoxy to phosphorus that can range from 10 : 1 to 1 : 1, more preferably from 6 : 1 to 2 : 1, and most preferably from 5 : 1 to 3 : 1.

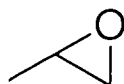
20 For the various embodiments, such a phosphorus-containing epoxy resin can be represented by a compound of Formula (I):

(Formula I)



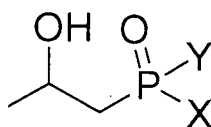
wherein each Z is independently a compound of Formula (II):

25 (Formula II)



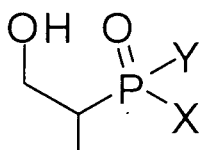
, a compound of Formula (III):

5 (Formula III)



, or a compound of Formula (IV):

(Formula IV)



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wherein each R_1 and R_2 is independently hydrogen or an alkyl moiety, R is a cycloaliphatic diradical, a bicyclic aliphatic diradical, or a tricyclic aliphatic diradical that contains from 6 to 30 carbons, and each Y and X is independently hydrogen, an aliphatic moiety having 1 to 20 carbon atoms, or an aromatic hydrocarbon moiety having 6 to 20 carbon atoms. For the various embodiments, the phosphorus-containing epoxy resin can be formed by reacting a phosphorus compound containing a phosphorus-hydrogen moiety and an epoxy resin.

For the embodiments, examples of the phosphorus compound containing a phosphorus-hydrogen moiety include, but are not limited to, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO); 1,3,2-dioxaphosphorinane; 2-hydroxy-5,5-dimethyl-; 1,3,2-dioxaphosphorinane; 1,3,2-dioxaphospholane; 1,3,2-dioxaphospholane; 2-oxide; 5,5-dimethyl-; 1,3,2-benzodioxaphosphole; 2-oxide; 1,3,2-benzodioxaphosphole; 1,3,2-diazaphospholidine; 1,3-dimethyl-; 1,3,2-diazaphospholidine; 1,3-dimethyl- and 2-oxide. For the embodiments, DOPO is the preferred phosphorus compound used in the present disclosure.

For the embodiments, R_1 and R_2 can be alkyl moieties that are saturated linear or branched monovalent hydrocarbon groups optionally containing oxygen. For the embodiments, the alkyl moieties can include carbon atoms within a range of from 1 to 20, preferably within a range of from 1 to 4. Examples of alkyl moieties include, but are not limited to, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl, and methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy,

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- 5 sec-butoxy, tert-butoxy, methoxymethyl, ethoxymethyl, iso-propoxymethyl, and butoxymethyl.

For the embodiments, examples of the cycloaliphatic diradicals, bicyclic aliphatic diradicals, and tricyclic aliphatic diradicals for R include, but are not limited to, a compound of Formula (A):

- 10 (Formula A)



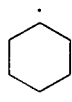
a compound of Formula (B):

(Formula B)



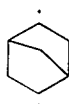
- 15 a compound of Formula (C):

(Formula C)



a compound of Formula (D):

- 20 (Formula D)



a compound of Formula (E):

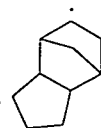
(Formula E)



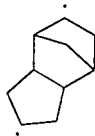
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a compound of Formula (F):

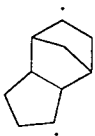
(Formula F)



- 5 a compound of Formula (G):
(Formula G)

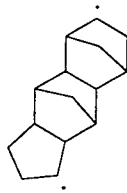


- a compound of Formula (H):
(Formula H)

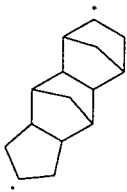


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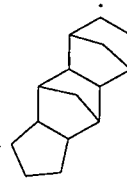
- a compound of Formula (I):
(Formula I)



- 15 a compound of Formula (J):
(Formula J)



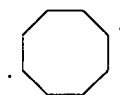
- a compound of Formula (K):
(Formula K)



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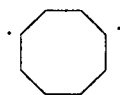
- a compound of Formula (L):
(Formula L)

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a compound of Formula (M):

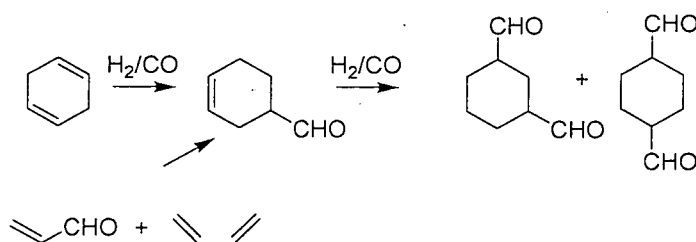
(Formula M)



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and mixtures thereof. For the embodiments, R is preferably a mixture of 1,3- and 1,4-cyclohexylidene (*e.g.*, compounds of Formulas (B) and (C)) or a mixture of bicyclic $C_{10}H_{14}$ diradicals (*e.g.*, compounds of Formulas (F), (G) and (H)) and can be prepared by one of two conversion pathways. The first pathway is hydroformylation of dienes which proceeds in two steps whereby an olefin-aldehyde is formed in the first step followed by formation of a dialdehyde. The second pathway is to form the olefin-aldehyde by a Diels-Alder reaction of acrolein with a diene followed by hydroformylation as shown in one specific example below.



20

As can be recognized by those skilled in the art, these hydroformylations give a mixture of isomers of the dialdehydes. The dialdehydes can then be converted by a condensation reaction with phenols to the compounds of Formula I where Z is hydrogen.

25

Examples of X and Y in the compound of Formula III and the compound of Formula IV can include, but are not limited to, hydroxy, methyl, methoxy, ethyl, ethoxy, propyl, propoxy, phenyl, phenoxy, -SH, thiomethyl, thioethyl, and thiophenyl. For the embodiments, X and Y can also be derived from DOPO.

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For the embodiments, the phosphorus-containing epoxy resin is formed by reacting a phosphorus compound that contains a phosphorus-hydrogen moiety, *e.g.*, DOPO, with an epoxy resin with a functionality of at least 3 by epoxidizing a reaction product of the condensation of phenol and the dialdehyde. For the embodiments, the epoxy resin formed by epoxidizing the reaction product of the condensation of phenol and the dialdehyde preferably has a polydispersity (M_w/M_n ; M_w equals weight

5 average molecular weight and Mn equals number average molecular weight) that is no greater than 2, preferably not higher than about 1.8, more preferably not higher than 1.5, and most preferably not higher than 1.3. The average number of hydroxyl groups per molecule of the reaction products can be within a range of from 4.0 to 6.0, preferably within a range of from 4.5 to 5.0.

10 For the embodiments, the dialdehydes that can be used in the condensation include, but are not limited to, dialdehydes of a cycloalkane having carbon atoms within a range of from 5 to 24, more preferably within a range of from 6 to 20, and most preferably within a range of from 6 to 15. Examples include, but are not limited to, dialdehydes of cyclohexane, cyclooctane, cyclododecane, norbornane, octahydro-
15 4,7-methano-1H-indene (saturated dicyclopentadiene), dodecahydro-4,9:5,8-dimethano-1H-benz[f]indene (saturated tricyclopentadiene). For example, the condensation can include condensing cyclohexane dicarboxaldehyde with phenol. For the embodiments, the cycloalkane dicarboxaldehyde may comprise one or more isomers (including regioisomers and stereoisomers) of a specific dicarboxaldehyde. For example, in the case of cyclohexane dicarboxaldehyde isomers, one or more of
20 cis-cyclohexane-1,3-dicarboxaldehyde, trans-cyclohexane-1,3-dicarboxaldehyde, cis-cyclohexane-1,4-dicarboxaldehyde and trans-cyclohexane-1,4-dicarboxaldehyde may be employed. However, it is also possible to employ cis and/or trans-cyclohexane-1,2-dicarboxaldehyde. Additionally, a mixture of two or more dicarboxaldehydes
25 which differ in the number of ring carbon atoms and/or in the presence or absence, number and/or types of ring substituents, *e.g.*, a mixture of one or more cyclohexane dicarboxaldehyde isomers and one or more cyclooctane dicarboxaldehyde isomers, may be employed in the process of the present disclosure.

For the embodiments, the condensation produces a reaction product that can
30 include a mixture of polyphenolic compounds. For the embodiments, the reaction product is epoxidized by using processes that include, but are not limited to, reacting with epichlorohydrin to form the polyglycidyl ether. For the embodiments, the hydroxy groups on the reaction products are converted into glycidyl ether groups to produce a polyglycidyl. The epoxidation produces a polyglycidyl ether having a
35 functionality of within a range of from 4 to 10, more preferably within a range of from 5 to 8, and most preferably within a range of from 6 to 7. For the embodiments, a percentage of hydroxy groups converted into glycidyl ether groups can be at least

- 5 90%, preferably at least 95%, more preferably at least 98%, and even more preferably at least 99% or above based on the number of hydroxy groups.

For the embodiments, the phenolic compound used in the condensation can be phenol (unsubstituted). Additionally, the aromatic ring of phenol may include one or more substituent's including, but not limited to, cyano, nitro, hydroxyl, unsubstituted
10 or substituted alkyl having 1 to 6 carbon atoms, unsubstituted or substituted cycloalkyl having carbon atoms within a range of from 5 to 8, unsubstituted or substituted alkoxy having carbon atoms within a range of from 1 to 6, unsubstituted or substituted alkenyl having carbon atoms within a range of from 3 to 6, unsubstituted or substituted alkenyloxy having carbon atoms within a range
15 of from 3 to 6, unsubstituted or substituted aryl having carbon atoms within a range of from 6 to 10 carbon, unsubstituted or substituted aralkyl having carbon atoms within a range of from 2 to 7, unsubstituted or substituted aryloxy having carbon atoms within a range of from 6 to 10, and unsubstituted or substituted aralkoxy having carbon atoms within a range of from 7 to 12. For the
20 embodiments, a molar ratio of the phenolic compound to the cycloalkane dicarboxaldehyde used in the condensation can be within a range of from 4 : 1 to 20 : 1, preferably within a range of from 5 : 1 to 15 : 1, and more preferably within a range of 6 : 1 to 12 : 1.

For the embodiments, the polyglycidyl ether is reacted with DOPO yielding the
25 phosphorus-containing epoxy resin of the present disclosure. A portion of the epoxy groups of the polyglycidyl ether are replaced with a phosphorus-hydrogen moiety when the polyglycidyl ether reacts with the DOPO. As DOPO is introduced, the functionality of epoxy resins will decrease as each molecule of DOPO reacts with an epoxy group, thereby removing that epoxy group for cross linking during curing.
30 Therefore, as the amount of DOPO reacting with epoxy resins increases, the crosslink density of a cured epoxy resin and the glass transition temperature can both decrease. In contrast, the present disclosure reacts a polyglycidyl ether having a functionality within a range of from 4 to 10, more preferably within a range of from 6 to 7, with DOPO and can maintain a functionality of greater than 3, allowing the glass transition
35 temperature to increase along with maintaining the crosslink density of the cured epoxy. Thus, the phosphorus-containing epoxy resin of the present disclosure can

- 5 have an increased glass transition temperature as compared to incumbent novolac-based epoxy resins.

Reacting the polyglycidyl ether with a phosphorus compound containing phosphorus-hydrogen moieties forms the phosphorus-containing epoxy resin of the present disclosure and can make it useful in the preparation of flame resistant

10 materials. The phosphorus-containing epoxy resin of the present disclosure can have a phosphorous content within a range of from 2 wt% to 20 wt%, more preferably within a range of from 4 wt% to 15 wt%, and most preferably within a range of from 5 wt% to 15 wt%. The embodiments of the present disclosure can also be useful in other applications requiring flame resistant materials, including semiconductor

15 packaging applications, electrical and electronic applications, and composite applications. In addition, the phosphorus-containing epoxy resin is substantially free of both bromine atoms and of halogen atoms.

For the various embodiments, the reaction of the phosphorus-containing epoxy resin with the phosphorus compound containing the phosphorus-hydrogen moiety,

20 *e.g.*, DOPO, is preferably carried out without the presence of water (generally the water is present in less than 5 wt%, more preferable less than 3 wt%, and most preferable less than 1 wt% based on the total weight of the curable composition) because water may tend to react with the DOPO and cause foaming. Water can be removed using well-known methods such as heating in a stream of dry air or nitrogen,

25 in a vacuum oven, or by azeotropic removal of water using an organic liquid such as hexane or toluene. This can be done either on the DOPO itself or on the mixture before reaction.

The present disclosure also provides curable compositions formed with the phosphorus-containing epoxy resin. The curable compositions of the present

30 disclosure can have a phosphorus content within a range of from 0.5 wt% to 5.0 wt% based on a total weight of the curable composition. The curable compositions of the present disclosure described herein may also optionally make use of at least one curing agent (also referred to as a "hardener") and/or curing accelerator. Examples of suitable curing agents include, but are not limited to, amine-curing agents such as

35 dicyandiamide, diaminodiphenylmethane and diaminodiphenylsulfone, polyamides, polyaminoamides, polyphenols, polymeric thiols, polycarboxylic acids and anhydrides such as phthalic anhydride, tetrahydrophthalic anhydride (THPA), methyl

5 tetrahydrophthalic anhydride (MTHPA), hexahydrophthalic anhydride (HHPA),
methyl hexahydrophthalic anhydride (MHHPA), nadic methyl anhydride (NMA),
polyazealic polyanhydride, succinic anhydride, and maleic anhydride styrene-maleic
anhydride copolymers. Additionally, phenolic curing agents such as phenol novolacs,
cresol novolacs, and bisphenol A novolacs may also be used. Curing agents are
10 preferably used in an amount of within a range of from 2 wt% to 80 wt%, based on
the total weight of the curable composition.

Curing accelerators (or catalysts) include substituted or epoxy-modified
imidazoles such as 2-methylimidazole, 2-phenyl imidazole and 2-ethyl-4-methyl
imidazole. Other heterocyclic amines such as 1,8-diazabicyclo[5.4.0]undec-7-ene
15 (also known as DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (also known as DBN)
may also be used. Tertiary amines and phosphines including, but not limited to,
triethylamine, tripropylamine, tributylamine, and triphenyl phosphine may also be
used. Additionally, phosphonium salts such as ethyltriphenylphosphonium acetate,
ethyltriphenylphosphonium acetate and ammonium salts such as
20 benzyltrimethylammonium acetate and benzyltrimethylammonium hydroxide can also
be employed as curing accelerators. Halogen salts (iodide, bromide, chloride, and
fluoride) are also usable, but are generally less desirable in halogen-free applications.
Catalysts are preferably used in an amount of within a range of from 0.05 wt% to
about 2.00 wt%, based on the total weight of the curable composition.

25 For the embodiments, the optimum ratio of the curing agent to the
phosphorus-containing epoxy is usually expressed in terms of equivalent ratio. There
can be a 1.00 : 1.00 equivalent ratio of epoxy to reactive hydrogen (-SH, -OH, -NH,
or -COOH) or anhydride in the curing agent. The curable compositions of the present
disclosure are preferably prepared with an equivalent ratio from 1.20 : 1.00 to 1.00 :
30 1.20, more preferably within a range of from 1.10 : 1.00 to 1.00 : 1.10, and most
preferably within a range of from 1.10 : 1.00 to 1.00 : 1.05

Generally, curing the curable composition formed with the phosphorus-
containing epoxy resin of Formula (I), in accordance with the disclosure, can be
carried out by first melting the phosphorus-containing epoxy resin in the curable
35 composition to obtain a homogeneous melt or dissolving it in a suitable solvent.
Examples of suitable solvents include, but are not limited to, alcohols such as
Dowanol™ PM (The Dow Chemical Company), ketones such as acetone and/or

5 methyl ethyl ketone, esters, and/or aromatic hydrocarbons. For the embodiments, the solvent can be used in an amount up to 50 wt% based on the total weight of the curable composition. The solvent can be removed by distillation or simple evaporation during the course of or at the end of the cure.

For the embodiments of the present disclosure, the curable compositions
10 formed with the phosphorus-containing epoxy resin can also include at least one of a composition component. For the various embodiments, the composition component of the curable composition can either be reactive or non-reactive with the phosphorus-containing epoxy resin of the present disclosure. For the various embodiments, curable compositions formed with the phosphorus-containing epoxy resin and the
15 composition component can be obtained by combining, mixing and then reacting the phosphorus-containing epoxy resin of the present disclosure with the at least one composition component. Examples of such composition components include, but are not limited to, epoxy resins, polyepoxide resins, cyanate esters, dicyanate esters, polycyanate esters, cyanate aromatic esters, maleimide resins, thermoplastics
20 polymers, polyurethanes, polyisocyanates, benzoxazine ring-containing compounds, unsaturated resin systems containing double or triple bonds, and combinations thereof.

In an additional embodiment, the curable compositions of the present disclosure can be formed with the phosphorus-containing epoxy resin of the present
25 disclosure and at least one reactive and/or non-reactive thermoplastic resin. Examples of such thermoplastic resins include, but are not limited to, polyphenylene oxide, polyphenylsulfones, polysulfones, polyethersulfones, polyvinylidene fluoride, polyetherimide, polyphthalimide, polybenzimidazole, acrylics, phenoxy, and combinations or blends thereof.

30 For the various embodiments, the phosphorus-containing epoxy resin of the present disclosure can be mixed with thermoplastic resin to form a hybrid crosslink network. Preparation of the curable compositions of the present disclosure can be accomplished by suitable mixing means known in the art, including dry blending the individual components and subsequently melt mixing, either directly in the extruder
35 used to make the finished article or pre-mixing in a separate extruder.

When softened or melted by the application of heat, the curable composition formed with the phosphorus-containing epoxy resin of the present disclosure and the

5 thermoplastic resin can be formed or molded using conventional techniques such as compression molding, injection molding, gas assisted injection molding, calendaring, vacuum forming, thermoforming, extrusion and/or blow molding, alone or in combination. The curable composition formed with the phosphorus-containing epoxy resin of the present disclosure and the thermoplastic resin may also be formed, spun,
10 or drawn into films, fibers, multi-layer laminates or extruded sheets, or can be compounded with one or more organic or inorganic substances.

For the various embodiments, the phosphorus-containing epoxy resin can be used in combination with other epoxy resins in curable compositions to increase the thermal resistance of cured epoxies formed from the other epoxy resins. The other
15 epoxy resins used may include at least one epoxy resin and/or polyepoxide resin, where combinations of one or more of the epoxy resins and one or more of the polyepoxide resins are possible. Examples of such epoxy resins include, but are not limited to, those selected from halogen-free epoxies, phosphorus-free epoxies, brominated epoxies, and phosphorus-containing epoxies and mixtures thereof, epoxy
20 functional polyoxazolidone containing compounds, cycloaliphatic epoxies, glycidyl methacrylate/styrene copolymers, and the reaction product of liquid epoxy resins and tetrabromo bisphenol A resins. Additionally, glycidyl ethers of: phenol novolacs, cresol novolacs, "trisphenol" (tris-4-hydroxybenzene methane), bisphenol A novolacs, dicyclopentadiene bisphenol, 1,1,2,2-tetraphenolethane, hydroquinone, resorcinol,
25 catechol, bisphenol, bisphenol-A, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, tetrabromobisphenol A, phenol-hydroxybenzaldehyde resins, cresol-hydroxybenzaldehyde novolac, dicyclopentadiene-dimethylphenol novolac, and combinations thereof may be used.

A Lewis acid may also be employed in the compositions that include an epoxy
30 resin. The Lewis acid may include, for example, one or a mixture of two or more halides, oxides, hydroxides and alkoxides of zinc, tin, titanium, cobalt, manganese, iron, silicon, aluminum, and boron. Examples of such Lewis acids, and anhydrides of Lewis acids include boric acid, metaboric acid, optionally substituted boroxines (such as trimethoxy boroxine, trimethyl boroxine or triethyl boroxine), optionally
35 substituted oxides of boron, alkyl borates, boron halides, zinc halides (such as zinc chloride) and other Lewis acids that tend to have a relatively weak conjugate base.

5 The phosphorus-containing epoxy resin and/or curable compositions formed with the phosphorus-containing epoxy resin may be useful in the preparation of various articles of manufacture. Thus, the disclosure also includes prepregs of the above composition as well as shaped articles, reinforced compositions, laminates, electrical laminates, coating, molded articles, adhesives, composite products as
10 hereinafter described from cured or partially cured phosphorus-containing epoxy resin or compositions that include the phosphorus-containing epoxy resin of the disclosure. In addition, the compositions of the disclosure can be used for various purposes in the form of a dried powder, pellets, a homogeneous mass, impregnated products and/or compounds.

15 A variety of additional additives may be added to the curable composition of the present disclosure. Examples of these additional additives include fibrous reinforcement, fillers, pigments, dyes, thickening agents, wetting agents, lubricants, flame-retardants and the like. Suitable fibrous and/or particulate reinforcing materials include silica, alumina trihydrate, aluminum oxide, aluminum hydroxide oxide, metal
20 oxides, nano tubes, glass fibers, quartz fibers, carbon fibers, boron fibers, Kevlar fibers and Teflon fibers, among others. A size range for the fibrous and/or particulate reinforcing materials can include 0.5 nanometer (nm) to 100 μm . For the various embodiments, the fibrous reinforcing materials can come in the form of a mat, cloth or continuous fibers.

25 Embodiments of the curable compositions may also include at least one of a synergist to help improve the flame-out ability of the cured composition. Examples of such synergists include, but are not limited to, aluminum hydroxide, magnesium hydroxide, zinc borate, metal phosphinates such as Exolit® OP-930 (available from Clariant), and combinations thereof. In addition, embodiments of the curable
30 compositions may also include adhesion promoters, such as modified organosilanes (epoxidized, methacryl, amino), acetylacetonates, sulfur-containing molecules and combinations thereof. Other additives can include, but are not limited to, wetting and dispersing aids such as modified organosilanes, Byk® 900 series and W 9010 (Byk-Chemie GmbH), modified fluorocarbons and combinations thereof; air release
35 additives such as Byk® A530, Byk® A525, Byk® A555, and Byk® A 560 (Byk-Chemie GmbH); surface modifiers such as slip and gloss additives; mold release agents such as waxes; and other functional additives or prereacted products to

- 5 improve polymer properties such as isocyanates, isocyanurates, cyanate esters, allyl containing molecules or other ethylenically unsaturated compounds, acrylates and combinations thereof.

For the various embodiments, a resin sheet can be formed from the phosphorus-containing epoxy resin and/or curable compositions of the present disclosure. In one embodiment, a plurality of sheets can be bonded together to form a laminated board, where the sheets comprise at least one of the resin sheet. The phosphorus-containing epoxy resin and/or curable compositions formed with the phosphorus-containing epoxy resin can also be used to form a resin clad metal foil. For example, a metal foil, such as a copper foil, can be coated with the phosphorus-containing epoxy resin and/or curable compositions formed with the phosphorus-containing epoxy resin of the present disclosure. The various embodiments also include a multi layer board that can be prepared by coating a laminated substrate with the phosphorus-containing epoxy resin and/or compositions of the present disclosure.

For the various embodiments, the phosphorus-containing epoxy resin and/or curable compositions of the present disclosure can be applied to a substrate as a coating or adhesive layer. Alternatively, the phosphorus-containing epoxy resin and/or compositions of the present disclosure can be molded or laminated in the form of a powder, a pellet or impregnated in a substrate such as a fibrous reinforcement. The phosphorus-containing epoxy resin and/or curable compositions of the present disclosure can then be cured by the application of heat.

The heat necessary to provide the proper curing conditions can depend on the proportion of composition components constituting the curable composition and the nature of the composition components employed. In general, the curable composition of this disclosure may be cured by heating it at a temperature within the range of 25 °C to 250 °C, preferably 100 °C to 200 °C, although differing according to the presence of a curing agent or its amount, or the types of the composition components in the curable composition. The time required for heating can be 60 seconds to 24 hours, where the exact time will differ according to whether the curable composition is used as a thin coating or as molded articles of relatively large thickness or as laminates or as matrix resins for fiber reinforced composites, particularly for electrical and electronic applications, *e.g.*, when applied to an electrically nonconductive material and subsequently curing the curable composition.

5

EXAMPLES

The following examples are given to illustrate, but not limit, the scope of this disclosure.

Materials

Phenol, available from the Dow Chemical Company.

10

Cyclohexane dicarboxaldehyde, prepared as described in WO2001007382, which is incorporated herein by reference in its entirety.

UV-dye, Durite® SD-357B (tetraphenolethane), available from Hexion.

p-toluenesulfonic acid (PTSA) (0.207% by weight), available from Sigma Aldrich.

15

Boric acid, technical grade, (CAS# 10043-35-3), available from Sigma Aldrich

Methyl ethyl ketone (MEK), technical grade, available from The Dow Chemical Company.

9,10-dihydro-9-oxa-10-phosphaphenethrene-10-oxide (DOPO), available from Schill and Seilacher.

20

Catalyst, ethyltriphenylphosphonium acetate (CAS # 35835-94-0) (diluted to 70% solids in methanol), available from Alfa Aesar.

Curing agent, Rezicure™ 3026, available from SI Group.

Curing agent, Dowanol™ PM, available from The Dow Chemical Company.

25

Solvent, Dowanol™ PMA, available from The Dow Chemical Company.

Solvent, 2-methylimidazole (20 wt% in methanol), available from Sigma Aldrich.

Sodium bicarbonate (NaHCO₃), technical grade, available from Sigma Aldrich.

Epoxy Resin, XZ92530, available from The Dow Chemical Company.

30

Test MethodsGlass Transition Temperature (T_g)

The glass transition temperature was measured on a Q200 Differential Scanning Calorimeter from TA Instruments (New Castle, DE). The temperature of the sample was increased 10 °C per minute from 30 °C to 220 °C. T_{g1} is reported as the temperature at which the mid-point of the first-order transition is observed on the first temperature ramp. The temperature was maintained constant at 220 °C for 15 minute and then allowed to equilibrate at 30 °C. Again, the temperature of the sample

35

- 5 was increased 10 °C per minute from 30 °C to 220 °C. Tg₂ is reported as the mid-point temperature of the first-order transition. The temperature was maintained constant at 220 °C for 15 minute and then allowed to equilibrate at 30 °C. The temperature of the sample was increased 20 °C per minute from 30 °C to 220 °C. Tg₃ is reported as the mid-point temperature of the first-order transition.

10

Thermal Decomposition Temperature (Td)

The Td was measured on a Q5000 TGA from TA instruments (New Castle, DE). The Td is reported as the temperature at which 5 wt% of the sample mass has degrades.

- 15 Epoxy Equivalent Weight (EEW)

The EEW was determined according to ASTM D1652-04 entitled "Standard Test Method for Epoxy Content of Epoxy Resins."

UL-94 Vertical Flame Test

- 20 A 5 centimeter (cm) long x 1 cm wide x 1.5 millimeter (mm) thick 8-ply laminate sample is made and conditioned in a 105°C oven for 8 hours prior to analysis. The sample is supported in a vertical position and a flame is applied to the bottom of the sample. A first flame is applied for ten seconds and then removed until flaming stops at which time a second flame is reapplied for another ten seconds and then removed. Five samples are made and tested. The results are reported as a 1st Burn Time and a 2nd Burn Time and a UL94 rating is determined. The 1st Burn Time is the time (in seconds) it takes for the flaming to stop after the first flame has been removed. Similarly, the 2nd Burn Time is the time (in seconds) it takes for the flaming to stop after the second flame has been removed.

Examples

- 30 Formation of Reaction Products by Condensation of Phenol and Cyclohexane Dicarboxaldehyde

- 35 Phenol (598 grams (g), 6.36 moles (mol)) and cyclohexane dicarboxaldehyde (74.2 g, 0.53 mol, mixture of 1,3- and 1,4-isomers; ratio of phenolic groups to aldehyde groups equal 6 : 1, equivalent ratio of phenol to cyclohexane dicarboxaldehyde equal 3 : 1) were added together in a 1 liter (L) 5-neck reactor.

5 The mixture was agitated at 500 revolutions per minute (rpm) with a mechanical stirrer and heated to 50 °C. At 50 °C and atmospheric pressure, *p*-toluenesulfonic acid (PTSA) (1.3959 g total, 0.207 wt%) was added in six portions over 30 minutes. The temperature increased a few degrees with each PTSA addition. After the 6th PTSA addition, the temperature controller was set to 70 °C and vacuum was applied
10 to the reactor. The pressure of the reactor was gradually decreased to remove water from the reaction solution. Once the reflux stopped, the reactor was vented and water (48 g) was added. Water (79.0 g) and sodium bicarbonate (NaHCO₃, 0.6212 g) were added to neutralize the PTSA. When the reaction contents had cooled to room temperature, the entire contents was transferred to a 2-L separatory funnel. Methyl
15 ethyl ketone (500 milliliter (ml)) was added to the 2-L separatory funnel, and the contents were washed several times with water to remove PTSA-salt. The solvents and excess phenol were removed using a rotary evaporator, and the reaction product was poured onto aluminum foil. Ultraviolet spectrophotometric analysis provided a hydroxyl equivalent weight (HEW) of 118.64.

20

Preparation of the Polyglycidyl Ether by Epoxidation of Reaction Product

The reaction products formed above (107.5 g, 0.22 mol based on the assumption of 100 % tetraphenol of the above structure), epichlorohydrin (414.08 g, 4.51 mol; ratio of epoxy groups to phenolic groups equal equivalent ratio of
25 epichlorohydrin to polyphenolic compounds equal 5.1 : 1.0) and Dowanol® PM (79.4 g, 12.7 wt%) were added to a 1.5-L 5-neck reactor. The resulting solution was heated to 65 °C while being agitated at 650 rpm. Upon reaching 65 °C, vacuum (28.5 kilopascal (kPa)) was applied to the reactor and 50 wt% aqueous NaOH (72.9 g) was added to the reaction mixture over a period of 4 hours. Upon completion of the
30 addition, the reaction mixture was kept for an extra 15 minutes at 65 °C and then the entire reactor content was filtered to remove by-product salt. The filtrate was transferred to a 2-L separatory funnel, methyl ethyl ketone was added to the filtrate and the resultant mixture was extracted several times with water to remove residual salt. Thereafter, the washed solution was concentrated on a rotary evaporator to
35 remove unreacted epichlorohydrin.

Preparation of the Phosphorus-Containing Epoxy Resin (3.0 wt% phosphorus) by Reacting Polyglycidyl Ether with DOPO

5 The polyglycidyl ether (88.79 g) was added to a 250 ml round bottom flask equipped with condenser, mechanical stirrer, and thermocouple and heated to 120 °C under a nitrogen purge at 50 cubic centimeters per minute (cc/min) flow rate. Upon melting, the temperature was increased to 125 °C and Durite® SD-357B (1.39 g) was added and allowed to stir for 30 minutes. The reaction mixture was allowed to cool to 10 110 °C, and 9,10-dihydro-9-oxa-10-phospheneanthrene-10-oxide (DOPO, 12.3 g) was added and allowed to stir until completely homogeneous. A-1 catalyst (125 milligrams (mg)) was then added and the temperature was increased to and maintained at 170 °C for 30 minutes. After 30 minutes, another 12.3 g of DOP was added and stirred until completely homogeneous. The reaction mixture was then 15 stirred for 30 minutes after the homogeneous mixture formed.

Preparation of the Phosphorus-Containing Epoxy Resin (2.7 wt% phosphorus) by Reacting Polyglycidyl Ether with DOPO

20 The procedure from the preparation of the phosphorus-containing epoxy resin (3.0 wt% phosphorus) was repeated but with the following changes: use 21.4 g of DOPO.

Preparation of the Phosphorus-Containing Epoxy Resin (3.7 wt% phosphorus) by Reacting Polyglycidyl Ether with DOPO

25 The procedure from the preparation of the phosphorus-containing epoxy resin (3.0 wt% phosphorus) was repeated but with the following changes: use 31.2 g of DOPO.

Preparation of Examples 1 to 11

30 Examples 1 to 11 were prepared by forming the following curable compositions in Table 1. The phosphorus-containing epoxy resin (192.69 g) was added to a container capable of holding such an amount. A 50 wt% solution of Rezicure™ 3026 in Dowanol™ PMA (53.6 g) and a 20 wt% solution of 2-methylimidazole in methanol were added to the container holding the phosphorus- 35 containing epoxy resin. The amounts provided in Table 1 are a “percent solids basis” meaning that the weight of the solvent (Dowanol™ PMA) of Rezicure™ 3026 and the solution of 2-methylimidazole in methanol are ignored in the calculations.

5

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Phosphorus-containing epoxy resin (3.0% Phosphorus) (g)	10.00	10.00	10.00	10.00	-	-	-	-	-	-	-
Phosphorus-containing epoxy resin (2.7% Phosphorus) (g)	-	-	-	-	100.00	-	100.00	-	-	-	-
Phosphorus-containing epoxy resin (3.7% Phosphorus) (g)	-	-	-	-	-	100.00	-	100.00	10.00	10.00	2693.40
Cyclohexane Tetraphenol (g)	-	-	4.00	4.00	-	-	39.20	33.95	-	-	-
Rezicure™ 3026 (g)	2.87	2.87	-	-	28.05	23.80	-	-	-	-	-
Dicyandiamide (g)	-	-	-	-	-	-	-	-	0.23	0.27	504.90
Boric Acid (g)	-	0.05	-	0.05	-	-	-	-	-	-	-
Total Solids (g)	12.87	12.92	14.00	14.05	128.05	123.80	139.20	133.95	10.23	10.27	3198.30

The compositions of Example 1-10, were formed and agitated for 2 hours before being applied to woven glass forming hand paint samples. The hand paint samples were then partially cured by subjecting them to a 170 °C oven for a sufficient amount of time to reduce the reactivity of the curing agent to 80 seconds. The resulting "B-staged" prepregs were cut into 12 inch by 12 inch squares. Eight sheets of the prepreg were stacked and pressed forming laminate samples at a temperature of 200 °C and a pressure of greater than 23 atmospheres (atm) (2330 kPa) for a period of greater than 90 minutes. Example 11 was scaled to pilot plant scale on a Litzler Treater and formed into a laminate sample. The thermal properties of the laminate samples for Examples 1-11 were analyzed and shown in Table 2.

Table 2

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Tg1 (°C)	163.3	177.9	194.3	197.4	-	-	-	-	176.0	182.6	162.0
Tg2 (°C)	165.6	176.3	193.5	198.1	-	-	-	-	175.1	174.9	-
Tg3	-	-	-	-	158.6	149.6	163.9	169.2	172.9	174.6	-

(°C)												
Td (°C)	345.2	355.6	336.7	337.4	399.1	375.6	391.9	382.5	335.5	337.3	362.0	

Preparation of Comparative Examples A to C

Comparative Examples A to C were made by forming curable compositions with an epoxy resin (XZ92530) and hardeners. The formulations and amounts

illustrated in Table 3 are based on a percent solids basis.

Table 3

	Comparative Example A	Comparative Example B	Comparative Example C
XZ92530 (g)	10.00	10.00	10.00
Rezicure™ 3026 (g)	2.87	2.87	-
Dicyandiamide (g)	-	-	0.31
Boric Acid (g)	-	0.05	-
Total Solids (g)	12.87	12.92	10.31

The curable compositions of Comparative Examples A - C, were formulated and agitated for 2 hours before being applied to woven glass forming hand paint samples. The hand paint samples were then partially cured by subjecting them to a 170 °C oven for a sufficient amount of time to reduce the reactivity of the curing agent to 80 seconds. The resulting "B-staged" prepregs were cut into 12 inch by 12 inch squares. Eight sheets of the prepreg were stacked and pressed forming laminate samples at a temperature of 200 °C and a pressure of greater than 23 atmospheres (atm) (2330 kPa) for a period of greater than 90 minutes. The thermal properties of the laminate samples for Comparative Examples A-C were analyzed and shown in Table 4.

Table 4

	Comparative Example A	Comparative Example B	Comparative Example C
Tg1 (°C)	139.6	122.9	119.9
Tg2 (°C)	142.9	121.4	118.8
Tg3 (°C)	-	-	122.7
Td (°C)	357.7	356.3	339.6

Analysis of Thermal Properties

- 5 It can be seen from comparing Table 2 (Examples 1-11) with Table 4
(Comparative Examples A-C) that the sample laminates formed from the phosphorus-
containing epoxy resin of the present disclosure yield significantly higher Tg values.
For example, Examples 1-4 yield a Tg of at least 20 °C higher than the Comparative
Examples A and B and Examples 9 and 10 yield a Tg of at least 50 °C higher than the
10 Comparative Example C. Additionally, the thermal decomposition temperature (Td)
values between the Examples and Comparative Examples remain essentially
unchanged.

UL-94 Flame Test

- 15 Five runs were performed with the laminate samples for Examples 5 – 8.
Each Example was tested and the 1st Burn Time (in seconds), 2nd Burn Time (in
seconds) and the UL-94 rating are shown in Table 5.

Table 5

	Example 5		Example 6		Example 7		Example 8	
	1 st Burn Time (s)	2 nd Burn Time (s)	1 st Burn Time (s)	2 nd Burn Time (s)	1 st Burn Time (s)	2 nd Burn Time (s)	1 st Burn Time (s)	2 nd Burn Time (s)
Run 1	9.5	11.0	7.4	6.5	19.6	0.0	8.6	0.0
Run 2	13.1	0.0	6.9	5.7	14.5	0.0	17.7	0.0
Run 3	11.0	5.3	8.6	6.3	19.4	0.0	6.7	13.9
Run 4	8.1	7.3	7.7	6.2	22.5	0.0	14.4	0.0
Run 5	7.8	11.6	6.4	5.6	17.8	4.0	14.3	1.7
UL 94 Rating	V-1		V-1		V-1		V-1	

- 20 As seen in Table 5, each run for the laminate samples for Examples 5 – 8
resulted in a UL 94 rating of V-1. Without a flame retardant, these samples would
“burn to the clamp” after the first exposure to the flame and is designated as
“unrated.” The V-1 rating for Examples 5 through 8 indicates that the flame retardant
such as phosphorus is active. In addition, the V-1 rating is acceptable for some
25 applications in some countries.

The laminate sample prepared from Example 11 (1.3-1.5 mm thick) was also
tested under the UL-94 Flame test. The burn times and the UL-94 rating are shown in
Table 6.

5

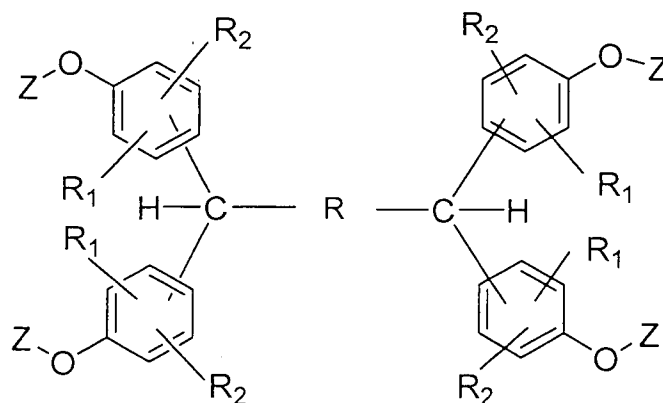
Table 6

	Example 11	
	1 st Burn Time (s)	2 nd Burn Time (s)
Run 1	1.8	4.9
Run 2	0.6	1.2
Run 3	1.0	0.9
Run 4	1.1	2.4
Run 5	3.3	1.5
Total Burn Time	7.8	10.9
1 st Burn + 2 nd Burn Time	18.7	
UL94 Rating	V-0	

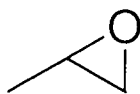
The results for Example 11 are significantly better (indicated by shorter burn times), and the samples achieve the more stringent rating of V-0. The V-0 rating is one standard for electronic applications in the United States.

We Claim:

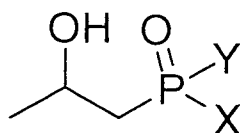
1. A phosphorus-containing epoxy resin of a compound of Formula (I):
(Formula I)



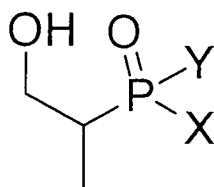
wherein each Z is independently a compound of Formula (II):
(Formula II)



, a compound of Formula (III):
(Formula III)



, or a compound of Formula (IV):
(Formula IV)



wherein:

each R_1 and R_2 is independently hydrogen or an alkyl moiety;

R in the compound of Formula I is a cycloaliphatic diradical, a bicyclic aliphatic diradical, or a tricyclic aliphatic diradical having 6 to 30 carbons; and

each Y and X is independently hydrogen, an aliphatic moiety having 1 to 20 carbon atoms or an aromatic hydrocarbon moiety having 6 to 20 carbon atoms.

2. The phosphorus-containing epoxy resin of claim 1, wherein R in the compound of Formula (I) is a mixture of 1,3- and 1,4-cyclohexylidene.
3. The phosphorus-containing epoxy resin of claim 1, wherein R in the compound of Formula (I) is a mixture of bicyclic $C_{10}H_{14}$ diradicals.
4. The phosphorus-containing epoxy resin of claim 1, wherein Y for the compound of Formula (III) and the compound of Formula (IV) is 2-biphenyl-2'-oxy, forming a tricyclic structure.
5. The phosphorus-containing epoxy resin of claim 1, wherein X in the compound of Formula (III) and the compound of Formula (IV) is methoxy.
6. The phosphorus-containing epoxy resin of claim 1, having a phosphorus content within a range of from 2 weight percent to 20 weight percent based on a total weight of the phosphorus-containing epoxy resin.
7. The phosphorus-containing epoxy resin of claim 1, wherein the phosphorus-containing epoxy resin has a molar ratio of epoxy to phosphorus is within a range of from 10 : 1 to 1 : 1.
8. A curable composition, comprising the phosphorus-containing epoxy resin of claims 1-7.

9. The curable composition of claim 8, wherein the curable composition has a phosphorus content within a range of from 0.5 weight percent to 5 weight percent based on a total weight of the curable composition.
10. A cured epoxy, formed with the phosphorus-containing epoxy resin of any one of claims 1-7.
11. The cured epoxy of claim 10, wherein the cured epoxy has a glass transition temperature of within a range of from 150 degrees Celsius to 200 degrees Celsius.
12. The cured epoxy of claim 10, wherein the cured epoxy has glass transition temperature of within a range of 170 degrees Celsius to 200 degrees Celsius.
13. A process for making the phosphorus-containing epoxy resin, comprising:
providing a polyglycidyl ether with a functionality at least 4 by epoxidizing a reaction product of a condensation of phenol and a dialdehyde; and
reacting the polyglycidyl ether with a phosphorus compound that contains a phosphorus-hydrogen moiety.
14. The process of claim 13, where the epoxy resin has a polydispersity of less than 2.0.
15. The process of claim 13, where the dialdehyde is cycloalkane dicarboxaldehyde.
16. The process of claim 13, where the phosphorus compound is 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide.