

FLAME RETARDANT COMPOSITION

Background of the Invention

5 The present invention relates to epoxy resin compositions and in particular to curable epoxy resin compositions for use in electrical laminate applications and electrical laminates prepared therefrom.

It is common practice to make electrical laminates and other fiber-reinforced composites
10 from a fibrous reinforcement and an epoxy- containing matrix resin. A typical example of a process for making such a laminate may comprise the following steps:

(1) An epoxy-containing formulation is applied to or impregnated into a substrate by rolling, dipping, spraying, other known techniques and/or combinations thereof. The
15 substrate is typically a woven or nonwoven fiber mat containing, for instance, glass fibers or paper. The epoxy resin formulation employed for impregnating is generally referred to as "varnish".

(2) The impregnated substrate is "B-staged" by heating at a temperature sufficient to draw
20 off solvent in the epoxy-containing formulation and optionally to partially cure the epoxy-containing formulation, so that the impregnated substrate can be handled easily. The "B-staging" step is usually carried out at a temperature of from 90°C to 210°C and for a time of from 1 minute to 15 minutes. The impregnated substrate that results from B-staging is generally referred to as a "prepreg". The temperature used for "B-staging" is most
25 commonly 100°C for composites and 130°C to 200°C for electrical laminates.

(3) One or more sheets of prepreg are stacked or laid up in alternating layers with one or more sheets of a conductive material, such as copper foil, if an electrical laminate is desired.

30 (4) The laid-up sheets are pressed at high temperature and pressure for a time sufficient to cure the resin and form a laminate. The temperature of this lamination step is usually between 100°C and 230°C, and is most often between 165°C and 200°C. The lamination step may also be carried out in two or more stages, such as a first stage between 100°C and 150°C and a second stage at between 165°C and 190°C. The pressure is usually between 50

N/cm² and 500 N/cm². The lamination step is usually carried out for a time of from 1 minute to 200 minutes, and most often for 45 minutes to 90 minutes. The lamination step may optionally be carried out at higher temperatures for shorter times (such as in continuous lamination processes) or for longer times at lower temperatures (such as in low energy press processes).

Optionally, the resulting laminate, for example, a copper-clad laminate, may be post-treated by heating for a time at high temperature and ambient pressure. The temperature of post-treatment is usually between 120°C and 250°C. The post-treatment time usually is between 30 minutes and 12 hours.

Various flame retardant additives are typically incorporated into the composition, such as bromine or phosphorous-containing components, in order to increase the flame retardancy of the final composition.

One type of flame retardant epoxy resin composition commonly used for electrical laminating applications comprises a brominated epoxy resin prepared from a diglycidyl ethers of bisphenol A and a tetrabromobisphenol A, dicyandiamide as a hardener, an organic solvent such as acetone, and an accelerator. The glass transition temperature of a cured epoxy resin prepared from such varnish compositions is undesirably low, for example from about 110°C to about 135°C. A low glass transition temperature results in a circuit board which is unsuitable for use at high temperatures.

A varnish composition for application to a reinforcing web used in the production of electrical laminates comprises a blend of a diglycidyl ether of bisphenol A and either bisphenol or tetrabromobisphenol A and a dicyandiamide as a hardener. The diglycidyl ether of bisphenol A is reacted in situ with bisphenol A and/or tetrabromobisphenol A and dicyandiamide during impregnation of the reinforcing web and the partial cure of the resin (see for example U.S. Pat. No. 3,738,862). This varnish composition leads to a laminate that also exhibits an undesirably low glass transition temperature (less than 135°C).

Another common material which is used in the electrical laminate industry is a so-called FR-4 (Flame resistant 4) resin. A FR-4 resin can be produced by reacting tetrabromobisphenol A and optionally bisphenol A with an excess of diglycidyl ether of

bisphenol A. The FR-4 resin is then formulated with solvents and dicyandiamide to produce a laminate. After complete reaction between the FR-4 resin and dicyandiamide, the laminate also exhibits an undesirably low glass transition temperature (usually between 130°C and 150°C).

5

However, there remains a need for further materials with higher glass transition temperatures. A high glass transition temperature is required because it provides a higher maximum operating temperature for the resultant printed circuit board.

- 10 A particularly preferred resin type for applications in which fire retardancy is important is a resin formed from bismaleimide, triazine cyanate ester and epoxy resin (referred to generally as "BT-epoxy resins"). Such materials are disclosed in U.S. Patent No. 4,100,364, U.S. Patent No. 4,456,712, Japanese Patent Application No. 55160021 and Japanese Patent Application No. 58138725.

15

Although materials with a high glass transition temperature are available, such materials usually show increased brittleness, and therefore reduced toughness. It is desirable to provide a material that not only has a high glass transition temperature, but also has improved toughness, as well as excellent flame retardancy.

20

Summary

Accordingly, in a first aspect of the present disclosure, there is provided a curable epoxy resin composition comprising:

- 25 (a) at least one oxazolidone-modified epoxy resin which is the reaction product of an epoxy resin and an isocyanate;
- (b) at least one maleimide;
- (c) at least one cyanate ester; and optionally
- (d) at least one non-oxazolidone containing epoxy resin,
- 30 wherein at least one component of the composition comprises halogen or phosphorous to provide flame retardancy to the cured composition. In a preferred embodiment, the oxazolidone-modified epoxy resin (a) comprises halogen or phosphorous to provide flame retardancy. In another preferred embodiment, the non-oxazolidone containing epoxy resin (d) comprises halogen or phosphorous to provide flame retardancy. In yet another preferred

embodiment, the non-oxazolidone containing epoxy resin (d) comprises halogen or phosphorous to provide flame retardancy and the oxazolidone-modified epoxy resin (a) is free or substantially free of halogen or phosphorous.

5 In a second aspect of the present disclosure, there is provided a method of making a curable epoxy resin composition comprising the step of mixing at least one oxazolidone-modified epoxy resin, which is the reaction produce of an epoxy resin and an isocyanate, with at least one maleimide and at least one cyanate ester to form a curable epoxy resin composition, wherein at least one component of the composition comprises halogen or phosphorous to
10 provide flame retardancy to the cured composition. In a preferred embodiment, the oxazolidone-modified epoxy resin (a) comprises halogen or phosphorous to provide flame retardancy. In another preferred embodiment, the non-oxazolidone containing epoxy resin (d) comprises halogen or phosphorous to provide flame retardancy. In yet another preferred embodiment, the non-oxazolidone containing epoxy resin (d) comprises halogen or
15 phosphorous to provide flame retardancy and the oxazolidone-modified epoxy resin (a) is free or substantially free of halogen or phosphorous.

In a third aspect of the present disclosure, there is provided a method of making a prepreg comprising the step of impregnating a reinforcing web with the above composition to form a
20 prepreg.

In a fourth aspect of the present disclosure, there is provide a method of making an electrical laminate comprising the steps of heating the above prepreg to a temperature sufficient to partially react the epoxy component of the composition with the maleimide and/or the
25 cyanate ester; laminating one or more layers of the prepreg with an electrically conductive material; and heating the so formed laminate at elevated pressure and elevated temperature to form an electrical laminate.

In a fifth aspect of the present disclosure, there is provided a curable epoxy resin composition comprising:
30

- (a) from 15 to 50 % by weight of at least one oxazolidone- modified epoxy resin which is the reaction product of an epoxy resin and an isocyanate;
 - (b) from 5 to 30 % by weight of at least one maleimide;
 - (c) from 10 to 40 % by weight of at least one cyanate ester;
 - (d) from 10 to 40 % by weight of at least one non-oxazolidone containing epoxy resin,
 - (e) at least one catalyst; and
 - (f) from 10 to 45 % by weight of at least one solvent,
- wherein at least one component of the composition comprises halogen or phosphorous to provide flame retardancy to the cured composition

In a sixth aspect of the present disclosure, there is provided an electrical laminate comprising the composition as defined above, wherein the laminate has an energy of delamination on impact of greater than 3 J.

In a seventh aspect of the present disclosure, there is provided an electrical laminate comprising the composition as defined above, wherein the laminate has an energy of delamination on impact of greater than 5 J.

In an embodiment of the present disclosure, there is provided the laminate produced by the above method. Preferably, the laminate has an energy of delamination on impact of greater than 3J, and more preferably greater than 5J, according to the test described in the Examples below.

In another embodiment of the present disclosure, there is provided the use of an oxazolidone-modified epoxy resin in an electrical laminate for improving the energy of delamination.

5 In an embodiment of the present disclosure, there is provided a composition as defined above having a glass transition temperature of at least 170°C when measured by Differential Scanning Calorimetry (DSC). In a yet further embodiment of the present disclosure, there is provided a composition having a flame retardancy of at least V-I of the UL94 test. Preferably, the composition of the first aspect of the disclosure has a glass transition temperature of at least 170°C when measured by Differential Scanning Calorimetry (DSC) and or a flame
10 retardancy of at least V- 1 of the UL94 test.

In a further embodiment of the present disclosure, there is provided an electrical laminate having an energy of delamination on impact of greater than 3J, preferably greater than 5J, according to the test described in the Examples below.

15

Detailed Description of the Invention

The oxazolidone-modified epoxy resin used in the present invention is formed by the partial reaction of at least one epoxy resin with at least one isocyanate. Oxazolidone groups are
20 also formed from the reaction of an epoxy resin with the cyanate ester. Although the presence of groups formed in this way is favourable, it is essential that at least some of the oxazolidone groups are formed by the reaction between epoxide and isocyanate. The partial reaction of the epoxy resin with the isocyanate must be undertaken prior to the use of the oxazolidone-modified epoxy resin in the composition of the present invention.

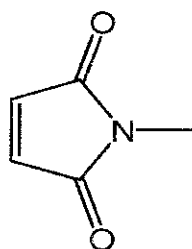
25

In a preferred embodiment, the composition comprises from about 2% to about 80%, preferably from about 5% to about 70%, more preferably from about 10% to about 60%, even more preferably from about 15% to about 50%, and most preferably from about 20% to about 40% by weight of the at least an oxazolidone-modified epoxy resin, obtained from
30 the reaction between an epoxy resin and an isocyanate.

Except where mentioned otherwise, all percentages are by weight based on the total formulation excluding solvents.

Preferably the oxazolidone-modified epoxy resin is an epoxy-terminated polyoxazolidone having from about 5% to about 30%, preferably from about 5% to about 20%, most preferably from about 10% to about 20% of isocyanate content, and having from about 50% to about 100%, preferably from about 75% to about 100%, most preferably more than about 90% of the original isocyanate groups converted to oxazolidone rings and from about 0% to about 50%, preferably from about 0% to about 25%, most preferably less than about 10% of the original isocyanate groups converted to isocyanurate rings.

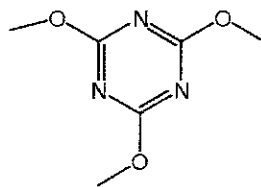
Suitably, the composition comprises about 2% to about 40%, preferably from about 5% to about 30%, more preferably from about 10% to about 25% by weight of the at least one maleimide. The maleimide compounds used in accordance with the present invention



contain at least one group of the formula

. The maleimide is preferably a bismaleimide.

The composition preferably comprises from about 2% to about 60%, preferably from about 5% to about 50%, more preferably from about 10% to about 40%, even more preferably from about 15% to about 35% by weight of the at least one cyanate ester. According to the present invention, a cyanate ester contains at least one group of the formula —OCN . Preferably the cyanate ester contains at least 2 cyanate ester groups per molecule on average. The cyanate ester is preferably partially trimerized to form triazine rings. A triazine



ring is described by the formula

. When the cyanate ester is partially

trimerized, from about 1 percent to about 70 percent, preferably from about 5 percent to about 60 percent, more preferably from about 20 percent to about 50 percent of the cyanate ester groups are polymerized to form triazines rings. The use of partially trimerized cyanate ester is especially suitable when the functionality of the cyanate ester contains between about 2 and about 3 cyanate ester groups per molecule on average, more particularly when

the cyanate ester contains about 2 cyanate ester groups per molecule on average. For example, a partially trimerized cyanate ester of bisphenol A is particularly suitable.

5 Optionally the maleimide and the cyanate ester resins may be partially reacted together prior to their inclusion in the composition of the present invention as described, for example, in U.S. Patent No. 4,456,712 and U.S. Patent No. 4,110,364.

10 The composition can comprise additional optional components, such as from about 10000 ppm to about 10 ppm, preferably from about 2000 ppm to about 50 ppm, more preferably from about 1000 ppm to about 100 ppm of at least one reaction catalyst based on the total weight of composition excluding solvent.

15 Preferably, at least one solvent is present in the composition. When present, the solvent is preferably used in an amount of from about 5% to about 50%, more preferably from about 10% to about 40%, most preferably from about 20% to about 35% based on the total weight of the formulation including solvent.

20 Optionally from about 1% to about 80%, preferably from about 5% to about 60%, more preferably from about 10% to about 40%, even more preferably from about 15% to about 30% of one or more epoxy resins that are not oxazolidone-modified can be used.

25 A further optional component is a vinylester, which, when present, is preferably used in an amount of from about 2% to about 40%, preferably from about 5% to about 30%, more preferably from about 10% to about 25% by weight.

A particularly preferred curable epoxy resin composition according to the present invention comprises (a) from 15 to 50 % by weight of at least one oxazolidone-modified epoxy resin which is the reaction product of an epoxy resin and an isocyanate;
30 (b) from 5 to 30 % by weight of at least one maleimide;
(c) from 10 to 40 % by weight of at least one cyanate ester;
(d) from 10 to 40 % by weight of at least one non-oxazolidone containing epoxy resin,
(e) at least one catalyst; and
(f) from 10 to 45 % by weight of at least one solvent,

wherein at least one component of the composition comprises halogen or phosphorous to provide flame retardancy to the cured composition. In a preferred embodiment, the oxazolidone-modified epoxy resin (a) comprises halogen or phosphorous to provide flame retardancy. In another preferred embodiment, the non-oxazolidone containing epoxy resin (d) comprises halogen or phosphorous to provide flame retardancy. In yet another preferred embodiment, the non-oxazolidone containing epoxy resin (d) comprises halogen or phosphorous to provide flame retardancy and the oxazolidone-modified epoxy resin (a) is free or substantially free of halogen or phosphorous.

- 10 The concentration of flame retardant is such that the composition is able to satisfy at least V-2, preferably at least V-1, more preferably at least V-0 of the UL94 test. Suitable flame retardants are known to the skilled person.

It is conventional in the preparation of epoxy-containing laminates to incorporate various additives in the composition to improve the flame-retardancy of the resulting laminate. Commonly, an additive is used which contains halogen or phosphorous groups. In a preferred embodiment, the oxazolidone-modified epoxy resin (a) comprises halogen or phosphorous to provide flame retardancy. Suitable halogen containing additives include for example tetrabromodiphenylolpropane, or epoxy resins prepared by reacting diglycidyl ether of bisphenol-A with tetrabromodiphenylolpropane.

Preferred halogenated flame retardants are brominated flame retardants. Examples of halogenated flame retardants include halogenated epoxy resins (especially brominated epoxy resins), tetrabromobisphenol A (TBBA) and its derivatives, D.E.R.542, D.E.R.560 which are available from The Dow Chemical Company, a brominated phenol novolac and its glycidyl ether, TBBA epoxy oligomer, and other derivatives. Examples of suitable additional flame retardant additives are given in a paper presented at "Flame retardants--101 Basic Dynamics--Past efforts create future opportunities", Fire Retardants Chemicals Association, Baltimore Marriot Inner Harbour Hotel, Baltimore Md., Mar. 24-27 1996.

Alternatively, the flame retardant compounds used in the composition of the present invention can be non-halogenated compound. Examples of suitable additional non-halogenated flame retardants are given in U.S. Patent No. 6,645,631 and WO 2005118604

A1, and the related references. Phosphorus based flame retardants are particularly preferred. For example EP-A-0384939, EP-A-0384940, EP-A-0408990, DE-A-4308184, DE-A-4308185, DE-A-4308187, WO-A-96/07685, and WO-A-96/07686 disclose the use of phosphorus flame retardants pre-reacted to form a di or multifunctional epoxy resin.

- 5 Alternatively, separate phosphorous containing components can be used such as phosphonic acid esters. A particularly preferred phosphorus-containing compound is 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOP) or its derivatives.

- 10 Optionally, at least one halogenated flame retardant and at least one non-halogenated flame retardant can be used in combination.

It is preferred that the flame retardant is incorporated in the reacted resin for example by providing reactive halide or phosphorous containing groups.

- 15 Typically, in order to reach the desired fire retardancy level (V-0 in the standard "Underwriters Laboratory" test method UL 94) for a brominated flame retardant, the bromine content is from about 40% to about 5%, preferably from about 30% to about 8%, more preferably from about 25% to about 10%, and even more preferably from about 20% to about 12% based on the total polymer weight in the product. In the case of a phosphorus-
- 20 containing flame retardant, the phosphorus content is from about 10% to about 0.2%, preferably from about 8% to about 0.5%, more preferably from about 5% to about 1%, and even more preferably from about 4% to about 1.5% based on the total polymer weight in the product.

- 25 In preferred embodiments, the flame retardant is present in at least one epoxy resin. The flame retardant can be in either the oxazolidone-modified epoxy resin, a non-oxazolidone modified epoxy resin, or both.

- Prepregs can be prepared by impregnating a supporting or reinforcing web with the above
- 30 epoxy resin composition (or varnish) by known methods such as those described in WO01/42359.

Although the amounts of the epoxy resin varnish composition which are applied to the reinforcing web will vary depending on the specific web and epoxy resin varnish

composition employed and the desired properties of the impregnated cloth and electrical laminates prepared therefrom, the epoxy resin varnish composition of the present invention is generally applied to the reinforcing web in conventional amounts. The resin content of the prepreg or laminate is from about 80% to about 20%, preferably from about 70% to about 30%, more preferably from about 65% to about 35%.

The impregnated web or prepreg is subsequently processed using conventional techniques. Such techniques involve advancing and/or curing the epoxy resin by heating the impregnated web to an elevated temperature such as from about 100°C to about 200°C. Subsequently, the prepreg is fabricated into laminates by laminating one or more prepreps, commonly cut to a predetermined size, with thin layers of an electrical conductive material such as copper foil using elevated temperatures and pressures. Conventionally, the laminating temperature varies from about 130°C to about 230°C, with pressures varying from about 34 kPa to about 6.9 MPa.

The glass transition temperature of the fully cured laminate prepared from above formulation is generally higher than 110°C, preferably higher than 150°C, more preferably higher than 170°C, even more preferably higher than 185°C when measured by Differential Scanning Calorimetry (DSC).

All of the various aspects and preferred embodiments of the invention can be used in any desired combination.

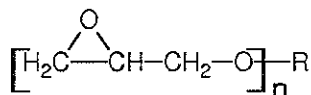
Suitable processes for the production of epoxy-terminated polyoxazolidones are disclosed for example in WO90/15089. The process comprises reacting the polyepoxide compound in an epoxy resin with a polyisocyanate compound in the presence of a catalyst for the reaction of the epoxy and isocyanate groups at an elevated temperature.

The polyepoxide compound useful for producing the oxazolidone-substituted epoxy resin is suitably a compound which possesses more than one 1,2-epoxy group. In general, the polyepoxide compound is saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compound which possesses more than one 1,2-epoxy group. The polyepoxide compound can be substituted with one or more substituents which are non-reactive with the

isocyanate groups such as lower alkyls and halogens. Such polyepoxide compounds are well known in the art. Illustrative polyepoxide compounds useful in the practice of the present invention are described in the Handbook of Epoxy Resins by H. E. Lee and K. Neville published in 1967 by McGraw-Hill, New York and U.S. Pat. No. 4,066,628.

5

Particularly useful polyepoxide compounds which can be used for the production of the oxazolidone-substituted epoxy resin are polyepoxides having the general formula



10

wherein R is substituted or unsubstituted aromatic, aliphatic, cycloaliphatic or heterocyclic polyvalent group and n had an average value of from 1 to less than 8. The preferred diepoxides include diglycidyl ether of 2,2-bis(4-hydroxyphenyl) propane (generally referred to as bisphenol A) and diglycidyl ether of 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane (generally referred to as tetrabromobisphenol A). Mixtures of any two or more polyepoxides can also be used in the practice of the present invention.

15

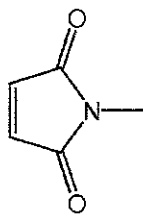
The polyisocyanate compound useful for reacting with the above polyepoxides is represented by the following general formula: $(\text{O}=\text{C}=\text{N})_m\text{---R}'$ wherein R' is substituted or unsubstituted aliphatic, aromatic or heterocyclic polyvalent group and m has an average value of greater than about 1 to less than about 5, preferably from about 1.5 to about 4, most preferably from about 2 to about 3. Examples of suitable polyisocyanates include 4,4'-methylene bis(phenylisocyanate) (MDI) and isomers thereof, higher functional homologues of MDI (commonly designated as "polymeric MDI"), toluene diisocyanate (TDI) such as 2,4-toluene diisocyanate and 2,6-toluene diisocyanate, m-xylylene diisocyanate, hexamethylene diisocyanate (HMDI) and isophoronediiisocyanate. Mixtures of any two or more polyisocyanates can also be used in the practice of the present invention. Other suitable polyisocyanate compounds are described in U.S. Pat. Nos. 3,313,747; 4,066,628 and 4,742,146.

25

Preferred polyisocyanate compounds are 4,4'-methylene bis(phenylisocyanate) (MDI) and isomers thereof, polymeric MDI and toluene diisocyanate (TDI). The most preferred polyisocyanate compounds are 4,4'-methylene bis(phenylisocyanate), isomers thereof and polymeric MDI.

30

The maleimide compounds used in accordance with the present invention contain at least



one group of the formula

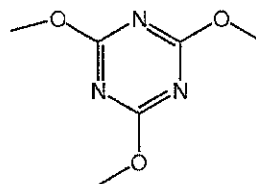
. The maleimides may be prepared by the reaction of

an unsaturated anhydride with the primary amino groups of an amine. The maleimide

compound of the present invention preferably has at least two maleimide groups. Suitable

- 5 maleimide compounds include e.g., 1-methyl-2,4-bismaleimidobenzene, N,N'-m-phenylenebismaleimide, N,N'-p-phenylenebismaleimide, N,N'-m-tolylenebismaleimide, N,N'-4,4-biphenylenebismaleimide, N,N'-4,4-(3,3'-dimethyl-biphenylene)bismaleimide, N,N'-4,4-(3,3'-diethyldiphenylmethane)bismaleimide, N,N'-4,4-(3,3'-diethyldiphenylmethane)bismaleimide, N,N'-4,4-diphenylmethanebismaleimide, 10 N,N'-4,4-diphenylpropane bismaleimide, N,N'-3,3'-diphenylsulfonebismaleimide, N,N'-4,4-diphenyl ether bismaleimide, 2,2-bis{4-(4-maleimidophenoxy)phenyl}propane, 2,2-bis{3-s-butyl-4,8-(4-maleimidophenoxy)phenyl}propane, 1,1-bis{4-(4-maleimidophenoxy)phenyl}decane, 4,4'-cyclohexylidene-bis{1-(4-maleimidophenoxy)phenyl}-2-cyclohexylbenzene, 2,2-bis{4-(4-maleimidophenoxy)phenyl}hexafluoropropane and the like. However, it is possible to use maleimide compounds with only one maleimide group. Other maleimides which are suitable will be known to the person skilled in the art and include those disclosed in, for example, U.S. Patent No. 5,189,116 and WO8700835.

- 20 According to the present invention, a cyanate ester contains at least one group of the formula -OCN . Preferably the cyanate ester contains at least 2 cyanate ester groups per molecule on average. The cyanate ester is preferably partially trimerized to form triazine



rings. A triazine ring is described by the formula

. Other cyanate

esters and triazines which are suitable will be known to the person skilled in the art and

- 25 include those disclosed in, for example, U.S. Patent No. 5,886,134 and EP 298742.

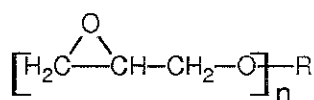
The additional non-oxazolidone containing epoxy resins optionally used in the curable epoxy resin composition are preferably polyepoxide compounds which are saturated or

unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compound which possesses more than one 1,2-epoxy group. The polyepoxide compound can be substituted with one or more substituents such as lower alkyls and halogens. Such polyepoxide compounds are well known in the art.

5

Illustrative polyepoxide compounds useful in the practice of the present invention are described in the Handbook of Epoxy Resins by H. E. Lee and K. Neville published in 1967 by McGraw-Hill, New York and U. S. Patent No. 4,066, 628.

- 10 Particularly useful polyepoxide compounds which can be used in the practice of the present invention are polyepoxides having the following general formula:



wherein R is substituted or unsubstituted aromatic, aliphatic, alicyclic, cycloaliphatic or heterocyclic polyvalent group and n had an average value of from 1 to less than 8.

15

Examples of epoxy resins that may be used include for example, the glycidyl ethers of resorcinol, catechol, hydroquinone, bisphenol, bisphenol A, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl ethane), bisphenol F, bisphenol K, tetrabromobisphenol A, phenol-formaldehyde novolac resins, bisphenol A-formaldehyde novolac resins, bisphenol F-formaldehyde novolac resins, alkyl substituted phenol-formaldehyde resins, phenol-hydroxybenzaldehyde resins, cresol-hydroxybenzaldehyde resins, dicyclopentadiene-phenol resins, dicyclopentadiene-substituted phenol resins tetramethylbisphenol, tetramethyl-tetrabromobisphenol, tetramethyltribromobisphenol, tetrachlorobisphenol A and any combination thereof.

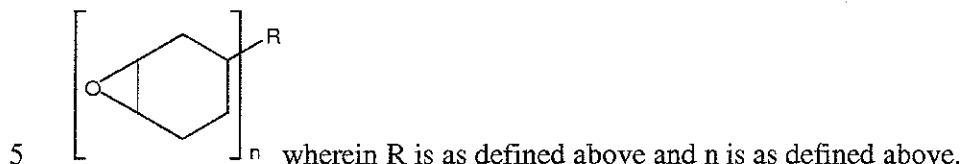
25

Examples of diepoxides which are particularly useful include diglycidyl ether of 2,2-bis (4-hydroxyphenyl) propane (generally referred to as bisphenol A) and diglycidyl ether of 2,2-bis (3,5-dibromo-4-hydroxyphenyl) propane (generally referred to as tetrabromobisphenol A).

30

Mixtures of any two or more non-oxazolidone containing polyepoxides can also be used.

Other useful epoxide compounds which can be used are cycloaliphatic epoxides. A cycloaliphatic epoxide consists of a saturated carbon ring having an epoxy oxygen bonded to two vicinal atoms in the carbon ring for example as illustrated by the following general formula:



The cycloaliphatic epoxide may be a monoepoxide, a diepoxide, a polyepoxide, or a mixture of those. For example, any of the cycloaliphatic epoxide described in U. S. Patent No. 3,686, 359 can be used.

10

The organic solvents suitably employed for the compositions of the present invention are those organic liquids in which the epoxy-terminated polyoxazolidone are soluble and which are sufficiently volatile such that they escape from the varnish composition before and/or during the partial cure and/or before the final cure. Illustrative examples of such organic liquids are various glycol ethers such as ethylene or propylene glycol monomethylether and the esters thereof such as ethylene glycol monomethylether acetate; ketones such as methylisobutyl ketone, methylethyl ketone, acetone and methylisopropyl ketone; and aromatic hydrocarbons such as toluene and xylene or mixtures thereof. Of such organic liquids, those preferably used as the solvent in the epoxy resin composition of the present invention are the ketones, particularly acetone, methyl ethyl ketone and methyl isobutyl ketone, or mixtures of these ketones with each other or with one or more of the other solvents. Other solvents that can be used are dimethyl sulfoxide (DMSO), N-methylpyrrolidone and dimethylformamide.

20

25

30

The amount of solvent most advantageously employed in the varnish of the present invention will vary depending on a variety of factors including the particular solvent, hardener and epoxy resin employed, desired properties of the epoxy resin composition (for example, desired viscosity of the varnish composition and the desired resin "pick-up" of this composition by the reinforcing web). Advantageously, the composition exhibits a viscosity from about 50 to about 1000 milliPascal seconds (mPa.s) measured using a Brookfield viscometer, Type RVT, 20 rpm and the appropriate spindle at 25°C. In general, the amount of solvent will range from about 5 to about 50, preferably from about 10 to about 45, more

preferably from about 15 to about 40 weight percent, based on the total weight of the varnish composition, the remainder comprising non-volatiles components (amount of the total solids other than the solvents). More preferably, the epoxy composition will contain from about 20 to about 40 weight percent of the solvent and from about 60 to about 80 weight percent non-volatiles.

The composition of the present invention preferably comprises at least one catalyst capable of promoting the curing of the different resins and promoting the reaction between the resins. Examples of suitable catalyst materials include metal catalysts such as zinc carboxylates, organozinc chelate compounds, and trialkyl aluminium, quaternary phosphonium and ammonium salts, tertiary amines and imidazole compounds. Preferably, the catalysts include a metal catalyst which contains one or more metals selected from the group consisting of chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, ruthenium, rhodium, palladium, tantalum, iridium, and platinum. Examples of suitable catalysts for the epoxy reaction are given in U.S. Patent No. 6,127,538. The catalyst of the present invention may be selected, for example, from the group consisting of amines, amides, substituted imidazoles, and non-substituted imidazoles, and the like, and combinations thereof. Examples of suitable catalyst compounds also include those compounds listed in European Patent Specification EP0954553,

Other catalysts useful in the present invention are phosphorus-containing compounds including, for example, triphenyl phosphine and phosphonium acid derivatives, and the like, and mixtures thereof. Particularly preferred catalysts are zinc-bis(2-ethylhexanoate) and copper acetylacetonate.

In addition, the compositions of the present invention may optionally comprise at least one vinyl ester.

The epoxy vinyl esters suitable for the practice of the present invention are generally prepared by the adduction of an at least difunctional epoxide with at least two molecules of an unsaturated monocarboxylic acid in which the carbon-to-carbon double bond is vinyl reactive. The epoxy vinyl ester is prepared by reacting the polyepoxide and the acid in about stoichiometric amounts, generally with heating and in the presence of a catalyst, such as a trivalent chromium salt, for example CrCl_3 , a phosphine, an onium salt, or a tertiary amine, for example, tris(N,N-dimethylaminomethyl phenol). Optionally, the epoxy vinyl

ester resin can be formed in the presence of a non-resinous, vinyl monomer such as styrene and the resulting mixture constitutes what is meant by the term epoxy vinyl ester resin.

Suitable non-resinous, vinyl monomers include, for example, styrene, alpha-methylstyrene, methylstyrene, divinylbenzene and acrylonitrile and others disclosed in U. S. Patent No.

5 4,824,919. A substantial number of different epoxy vinyl ester resins having distinct characteristics may be prepared by reacting different epoxides (or mixtures thereof) with various unsaturated acids (or mixtures thereof). Similarly, the properties of the epoxy vinyl ester resin/non-resinous vinyl monomer mixture may be varied by selecting various such monomers (or mixtures thereof). Examples of suitable vinyl esters are given in EP 927213
10 and WO9810004.

Optionally, the curable composition of the present invention may further contain other components typically used in thermosetting resin composition particularly for making prepregs and laminates; and which do not detrimentally affect the properties or performance
15 of the composition of the present invention, or the final cured product therefrom. For example, other optional components useful in the composition may include toughening agents, curing inhibitors, fillers, wetting agents, colorants, flame retardants, solvents, thermoplastics, processing aids, fluorescent compounds, such as tetraphenolethane (TPE) or derivatives thereof, UV blocking compounds, and other additives. The compositions of the
20 present invention may also include other optional constituents such as inorganic fillers and additional flame retardants, for example antimony oxide, octabromodiphenyl oxide, decabromodiphenyl oxide, phosphoric acid and other such constituents as is known in the art including, but not limited to, dyes, pigments, surfactants, flow control agents, plasticizers, and the like.

25 In one embodiment, the composition may optionally contain a toughening agent that creates phase-separated micro-domains. Preferably, the toughening agent creates phase-separated domains or particles, which average size is lower than about 5 micron, preferably lower than about 2 micron, more preferably lower than about 500 nm, and even more preferably
30 lower than about 100 nm. Preferably, the toughening agent is a block copolymer toughening agent, more preferably the toughening agent is a triblock toughening agent, or the toughening agent consists of pre-formed particles, preferably core-shell particles. In particular, the triblock copolymer could have polystyrene, polybutadiene, and poly(methyl methacrylate) segments or poly(methyl methacrylate) and poly(butyl acrylate) segments.

Preferably, the toughening agent does not substantially reduce Tg of the cured system, i.e. the reduction of Tg is less than 15°C, preferably less than 10°C, and more preferably less than 5°C. When present, the concentration of toughening agent is between about 0.1 and about 30 phr, preferably between about 0.5 and about 20 phr, more preferably between
5 about 1 and about 10 phr, and even more preferably between about 2 and about 8 phr.

In another embodiment, the epoxy resin composition may optionally contain a fluorescent and a UV blocking compound, such as tetraphenolethane. Preferably, the fluorescent compound is tetraphenol ethane (TPE) or derivatives. Preferably, the UV blocking
10 compound is TPE or derivatives.

In another embodiment, the composition of the present invention may contain a cure inhibitor, such as boric acid. In one embodiment, the amount of boric acid is preferably from about 0.01 to about 3% by weight to the epoxy resin (a) (based on solids), more
15 preferably from about 0.1 to about 2% by weight, and more preferably from about 0.2 to about 1.5% by weight. In this embodiment, it is particularly useful to maintain the presence of a portion of imidazole catalyst since boric acid forms complexes with imidazoles which act as a latent catalyst for the composition.

20 The compositions of the present invention are particularly useful in impregnating weaves, webs, fabric and cloth of variety of different materials including glass, quartz and synthetic fibers such as aramid. In the preparation of electrical laminates, a glass web is conventionally employed.

25 Preferred embodiments of the present invention will now be further described with reference to the following Examples.

Examples

30 The following Examples are set forth to illustrate various embodiments of the present invention; and are not intended to limit the scope of the present invention. Unless otherwise stated all parts and percentages in the Examples are by weight.

Various terms, abbreviations and designations for the raw materials used in the following Examples are explained as follows:

EEW stands for epoxy equivalent weight (on solids).

% Br stands for bromine content (by weight, on solids).

5 % P stands for phosphorus content (by weight, on solids).

Epoxy Resin F is a polymer of bisphenol A, tetrabromobisphenol A, and epichlorohydrin. It is a conventional brominated FR-4 epoxy resin, EEW = 450, %Br = 20%.

Epoxy Resin H is a polymer of tetrabromobisphenol A and epichlorohydrin. It is a high bromine content epoxy resin, EEW = 450, %Br = 49%.

10 Epoxy Resin O is a polymer of methylene diphenylene isocyanate, diglycidyl ether of bisphenol A, and diglycidyl ether of tetrabromobisphenol A. It is a brominated oxazolidone-modified epoxy resin and brominated epoxy resins, EEW = 360, %Br = 17%.

Epoxy Resin D is a conventional diglycidyl ether of bisphenol A, EEW = 180.

Epoxy Resin M is a polymer of methylene diphenylene isocyanate and diglycidyl ether of bisphenol A. It is a non-brominated oxazolidone-modified epoxy resin, EEW = 400.

Epoxy Resin P is a phosphorus-modified multifunctional polymeric epoxy resin. It is a halogen-free FR-4 epoxy resin, EEW = 325, % P = 3.0%.

Resin B is diphenylmethane-4,4'-bismaleimide.

Resin T is a triazine homopolymer of 2,2-bis(4-cyanatophenyl)propane

20 Catalyst is zinc-bis(2-ethylhexanoate).

MEK is methyl ethyl ketone.

DMF is N,N-dimethylformamide.

The glass reinforcement used in the Examples is a woven 7628-type E-glass.

25 The copper foil used in the Examples is a standard 35 micron (1 oz) grade.

The varnish formulations according to the present invention were prepared by dissolving the individual resins and catalyst components in suitable solvents at ambient temperature and mixing the solutions in accordance with the amounts set out in Table 1 below. The amounts of each epoxy resin component were chosen such that the Bromine content was identical in each composition. Prepregs were prepared by coating the varnish on style 7628 glass cloth and drying in a horizontal laboratory treater oven at 178° C for about 3 minutes to evaporate the solvents and advance the reacting mixture to a non-tacky B-stage. Laminates were prepared using 8 prepreg plies sandwiched between sheets of copper foil and pressing at

30

200°C for 90 minutes. The pressure applied to the laminate allows the amount of resin remaining on the laminate. In this case, the pressure was adjusted to provide a laminate resin content equal to about 43%.

5

Example 1 and Comparative Example A

Table 1

Varnish Composition Raw materials	Comparative Example A	Example 1
Epoxy Resin F [80% non volatiles in MEK]	176.9	0.0
Epoxy Resin H [70% non volatiles in DMF]	77.0	99.6
Epoxy Resin O [80% non volatiles in acetone]	0.0	126.0
Resin T [75% non volatiles in MEK]	100.0	100.0
Resin B [50% non volatiles in MEK]	100.0	100.0
Catalyst [10% non volatiles in MEK]	0.5	0.6
MEK	33.4	33.3

10

Table 2

Varnish Properties	Comparative Example A	Example 1
Varnish gel time	290	270
%Br (on non volatiles)	17%	17%
% non volatiles	65.7%	64.3%

Table 3

Test Results	Comparative Example A	Example 1
Colour	Homogenous dark brown	Homogenous dark brown
Tg (DSC, mid point, 20 °C/min), °C	190	205
Tt (DMTA, peak tan δ , 1 Hz), °C	212	227
Tg (TMA, 10 °C/min), °C	178	195
T288 (TMA), min	10	10
Average CTE 50 – 288 °C (TMA), ppm/K	150	105
UL 94, rating / sum of individual burning times	V-0, 11 s	V-0, 2 s
Water uptake (High Pressure Cooker, 2h, 121 °C), wt%	0.26	0.24
High Pressure Cooker 2h + 2 min dip @288 °C, %pass visual	100% pass	100% pass
Copper Peel Strength, 35 μ m standard copper, N/cm	13	13
Dk / Df measured at 1MHz	4.05 / 0.004	3.90 / 0.004
Dk / Df measured at 10MHz	4.00 / 0.006	3.90 / 0.006
Dk / Df measured at 100MHz	3.95 / 0.006	3.85 / 0.006
Dk / Df measured at 500MHz	3.90 / 0.006	3.80 / 0.006
Dk / Df measured at 1GHz	3.95 / 0.005	3.80 / 0.005
Energy of delamination on impact, J	2.7	6.2

- It can be seen that the Example of the present invention not only has a significantly higher glass transition temperature, but also an increase in energy of delamination and a decrease in Dk. The increase in glass transition temperature allows use of the laminate at higher operating temperatures. The increase in energy of delamination demonstrates that the resultant laminate is also tougher than the comparative example, and the reduction in dielectric constant is useful for high end printed circuit boards to ensure higher signal speed.

The results in Table 3 were obtained using the following test methods:

Table 4

5

Property Measured	IPC Test Method
Gel time, prepreg materials [prepreg gel time] Note: Similar method was used to determine varnish stroke cure gel time	IPC-TM-650-2.3.18A
Glass transition temperature and cure factor by DSC [Tg] Note: Tg was determined on laminates with a heating ramp of 20°C/min	IPC-TM-650-2.4.25C
Glass Transition and Modulus of Materials Used in High Density Interconnection (HDI) and Microvias - DMA Method [Tt] Note: Tt was reported as the transition peak temperature in the tanδ plot. The heating ramp consisted in 3°C increase steps followed by 20s dwell time.	IPC-TM-650-2.4.24.4, method
Glass transition temperature and z-axis Thermal expansion by Thermal Mechanical Analysis (TMA) [Coefficient of Thermal Expansion (CTE)]	IPC-TM-650-2.4.24C
Time to delamination (TMA Method) [T288] Note: T288 was measured at 288°C	IPC-TM-650-2.4.24.1
Thermal decomposition temperature [Td] by Thermo-Gravimetry Analysis (TGA) Note: Td was determined at 5% weight loss under nitrogen with a heating ramp of 10°C/min	IPC-TM-650-2.4.24.6
Flammability of laminate [UL94]	IPC-TM-650-2.3.10B
Pressure vessel method for glass epoxy laminate integrity [high pressure cooker test (HPCT)] Note: Laminates coupons were conditioned in the pressure vessel in a moisture-saturated atmosphere at 121 °C for 2h	IPC-TM-650-2.6.16
Peel strength of metallic clad laminates [copper peel strength (CPS)]	IPC-TM-650-2.4.8C
Permittivity and loss tangent from 1MHz to 1GHz with parallel plates at 25°C [Dk / Df]	IPC-TM-650-2.5.5.9

The energy of delamination on impact is the energy required to reach delamination of the laminate on an impact. The equipment used in this test is a Byk Chemie impact tester model N°5510. The indenter used is a steel punch (4 lb) with a hemispherical head (diameter = 5/8 inches). By gradually increasing the distance the weight drops, the height at which delamination occurs is determined (noted as Hd). The energy of delamination on impact (noted as Ed) is then calculated as follows:

10

$E_d = \text{mass} \times \text{distance} \times \text{acceleration}$

$E_d = 0.1781 \times H_d$, where H_d is measured in cm and E_d in joule.

The higher the value of E_d , the better the toughness of the laminate and the higher the interlayer adhesion. This is also a measure of brittleness. The higher the value of E_d , the lower the brittleness.

Example 2 and Comparative Example B

Table 5

Varnish Composition Raw materials	Comparative Example B	Example 2
Epoxy Resin D [100% non volatiles]	28.0	0.0
Epoxy Resin M [100% non volatiles]	0.0	28.0
Epoxy Resin P [75% non volatiles in MEK]	74.7	74.7
Resin T [75% non volatiles in MEK]	44.8	44.8
Resin B [50% non volatiles in MEK]	44.8	44.8
Catalyst [10% non volatiles in MEK]	0.35	0.35
MEK	13.3	13.3

Table 6

Varnish Properties	Comparative Example B	Example 2
Varnish gel time	325	330
% P (on non volatiles)	1.2	1.2
% non volatiles	68.0	68.0

Table 7

Test Results	Comparative Example B	Example 2
Colour	Homogeneous dark brown	Homogeneous dark brown
T _g (DSC, mid point, 10 °C/min), °C	150	175
T _d (TGA, 5% weight loss, 10 °C/min), °C	354	360
Energy of delamination on impact, J	1.8	6.2

It can be seen that the Example of the present invention not only has a significantly higher glass transition temperature, but also an increase in energy of delamination and a marginal

improvement in thermal decomposition temperature. The increase in glass transition temperature allows use of the laminate at higher operating temperatures. The increase in energy of delamination demonstrates that the resultant laminate is also tougher than the comparative example.

5

Example 3

Table 8

Varnish Composition Raw materials	Example 3
Epoxy Resin H [70% non volatiles in DMF]	55.0
Epoxy Resin O [80% non volatiles in acetone]	167.6
Resin T [75% non volatiles in MEK]	100.0
Resin B [50% non volatiles in MEK]	100.0
Catalyst [10% non volatiles in MEK]	0.6

Table 9

Varnish Properties	Example 3
Varnish gel time	305
% Br (on non volatiles)	14
% non volatiles	70.3

10

Table 10

Test Results	Example 3
Colour	Homogenous dark brown
Tg (DSC, mid point, 20°C/min), °C	205
UL 94, rating / sum of individual burning times	V-0, 7 s
Water uptake (High Pressure Cooker, 2h, 121 °C), wt%	0.22
High Pressure Cooker 2h + 2 min dip @288 °C, %pass visual	100% pass
Copper Peel Strength, 35µm standard copper, N/cm	15
Energy of delamination on impact, J	7.1

It can be seen that the higher concentration of oxazolidone-modified epoxy resin used in Example 3 leads to higher energy of delamination and higher copper peel strength when compared to Example 1.

- 5 It can also be seen that Example 3 of the present invention not only has a significantly higher glass transition temperature and energy of delamination when compared to Comparative Example A, but also requires lower concentration of bromine flame retardant to achieve similar (marginally better) flame retardancy.

Claims

1. A curable epoxy resin composition comprising:
 - (a) at least one oxazolidone-modified epoxy resin which is the reaction product of an epoxy
5 resin and an isocyanate;
 - (b) at least one maleimide;
 - (c) at least one cyanate ester; and optionally
 - (d) at least one non-oxazolidone containing epoxy resin,wherein at least one component of the composition comprises halogen or phosphorous to
10 provide flame retardancy to the cured composition.
2. A composition as claimed in Claim 1 additionally comprising a catalyst.
3. A composition as claimed in Claim 1 or Claim 2 additionally comprising a solvent.
15
4. A composition as claimed in any one of Claims 1 to 3 additionally comprising a vinyl ester.
5. A composition as claimed in any one of the preceding claims, wherein the
20 oxazolidone-modified epoxy resin is present in an amount of from 15 to 50 % by weight of the composition.
6. A composition as claimed in any one of the preceding claims, wherein the cyanate ester is present in an amount of from 10 to 40 % by weight of the composition.
25
7. A composition as claimed in any one of the preceding claims, wherein the cyanate ester comprises triazine rings.
8. A composition as claimed in any one of the preceding claims, wherein the maleimide
30 is present in an amount of from 5 to 30 % by weight of the composition.
9. A composition as claimed in Claim 8, wherein the maleimide is a bismaleimide.

10. A composition as claimed in Claim 3, wherein the solvent is present in an amount of from 10 to 40 % by weight.

11. A composition as claimed in any one of the preceding claims, wherein the non-oxazolidone containing epoxy resin is present in an amount of from 10 to 40 % by weight.

12. A composition as claimed in Claim 4, wherein the vinyl ester is present in an amount of from 5 to 30 % by weight.

13. A curable epoxy resin composition comprising:
(a) from 15 to 50 % by weight of at least one oxazolidone-modified epoxy resin which is the reaction product of an epoxy resin and an isocyanate;
(b) from 5 to 30 % by weight of at least one maleimide;
(c) from 10 to 40 % by weight of at least one cyanate ester;
(d) from 10 to 40 % by weight of at least one non-oxazolidone containing epoxy resin,
(e) at least one catalyst; and
(f) from 10 to 45 % by weight of at least one solvent,
wherein at least one component of the composition comprises halogen or phosphorous to provide flame retardancy to the cured composition.

14. A composition as claimed in any one of the preceding claims, wherein the composition has a glass transition temperature of at least 170°C when measured by Differential Scanning Calorimetry (DSC).

15. A composition as claimed in any one of the preceding claims, wherein the composition has a flame retardancy of at least V-1 of the UL94 test.

16. An electrical laminate comprising the composition of any one of claims 1 to 15, wherein the laminate has an energy of delamination on impact of greater than 3J.

17. An electrical laminate comprising the composition of any one of claims 1 to 16, wherein the laminate has an energy of delamination on impact of greater than 5J.

18. A method of making a curable epoxy resin composition comprising the step of:

mixing at least one oxazolidone-modified epoxy resin, which is the reaction produce of an epoxy resin and an isocyanate, with at least one maleimide and at least one cyanate ester to form a curable epoxy resin composition,

5 wherein at least one component of the composition comprises halogen or phosphorous to provide flame retardancy to the cured composition.

19. A method of making a prepreg comprising the steps of:

impregnating a reinforcing web with the composition of any one of Claims 1 to 17 to form a prepreg.

10

20. A method of making an electrical laminate comprising the steps of:

heating the prepreg of claim 19 to a temperature sufficient to partially react the epoxy component of the composition with the maleimide and/or the cyanate ester;

laminating one or more layers of the prepreg with an electrically conductive material; and

15 heating the so formed laminate at elevated pressure and elevated temperature to form an electrical laminate.

21. The composition of any one of the claims 1 to 15, wherein the oxazolidone-modified epoxy resin comprises halogen or phosphorous to provide flame retardancy.

20

22. The composition of any one of the claims 1 to 15, wherein the non-oxazolidone containing epoxy resin comprises halogen or phosphorus to provide flame retardancy.

23. The composition of claim 22, wherein the oxazolidone-modified epoxy resin is
25 free of halogen or phosphorus.