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(71) Applicant: SABIC GLOBAL TECHNOLOGIES B.V.

[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventor; and

(71) Applicant (for BZ only): VERGHESE, Nikhil K. E.

[US/US]; 14100 Southwest Freeway, Suite 600, Sugar Land, Texas 77478 (US).

(72) Inventor: AGRAWAL, Mukesh; Plot No. 81-85 Village:

Chikkadunnasandra, Anekal Taluk, Off. Sarjapura - Attibele Road, Bangalore, Karnataka 562125 (IN).

(74) Agent: WASSER, Ian M.; CANTOR COLBURN LLP, 20

CHURCH STREET, 22ND FLOOR, HARTFORD, Connecticut 06103 (US).

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(54) Title: CURABLE ENCAPSULANT INCLUDING THERMOSET EPOXY COMPOSITION

(57) Abstract: An electronic device encapsulated by a curable encapsulant composition, the curable encapsulant composition comprising: 100 parts by weight of an epoxy resin composition; 2 to 200 parts by weight of an aromatic dianhydride curing agent; an effective amount of a curing catalyst; and an additional curing promoter comprising a monoanhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, and wherein the curable encapsulant composition after curing has a glass transition temperature of 120 to 320°C, preferably 160 to 320°C, more preferably 180 to 320°C, even more preferably 200 to 320°C, still more preferably 250 to 320°C, as determined by dynamic mechanical analysis.



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CURABLE ENCAPSULANT INCLUDING THERMOSET EPOXY COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of and priority to European Patent Application No. 19184434.9, filed on July 4, 2019 and Indian Patent Application No. 201911008307, filed March 4, 2019, the entire contents of which are both incorporated by reference herein.

BACKGROUND

[0001] Thermoset polymers are used in a wide variety of consumer and industrial products including protective coatings, adhesives, electronic laminates (such as those used in the fabrication of printed circuit boards), electronic encapsulants (such as those used to protect semiconductors and integrated circuits), glass fiber-reinforced pipes, and automotive parts (such as leaf springs, pumps, and electrical components). Thermoset epoxies are derived from thermosetting epoxy resins that are polymerized in the presence of a co-reactive curing agent (also referred to in the art as a hardener), a catalytic curing agent (also referred to in the art as a cure accelerator or catalyst), or both, to afford a cured thermoset epoxy.

[0002] When thermoset epoxies are used to encapsulate high performance semiconductor devices, which can operate at temperatures that exceed 160°C, high temperature stability is necessary. However, conventional epoxy resins cured with amine or monoanhydride curing agents often lack high temperature stability, for example at temperatures higher than 220°C.

[0003] Accordingly, there remains a need for epoxy thermosetting encapsulants that demonstrate high temperature stability.

BRIEF DESCRIPTION

[0004] According to an aspect, an electronic device encapsulated by a curable encapsulant composition comprising 100 parts by weight of an epoxy resin composition; 2 to 200 parts by weight of an aromatic dianhydride curing agent; an effective amount of a curing catalyst; and an additional curing promoter comprising a monoanhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, and wherein the curable encapsulant composition after curing has a glass transition temperature of 120 to 320°C, preferably 160 to 320°C, more preferably 180 to 320°C, even more preferably 200 to 320°C, still more preferably 250 to 320°C, as determined by dynamic mechanical analysis.

[0005] According to another aspect, a method of encapsulating an electronic device with the curable encapsulation composition comprises combining the epoxy resin, the curing agent, and the curing catalyst under conditions effective to form a mixture; heating the mixture at a temperature sufficient to soften or liquefy the mixture; and encapsulating at least a portion of the electronic device.

[0006] In still another aspect, an electronic device comprising a cured product of the curable encapsulant composition is provided.

[0007] The above described and other features are exemplified by the following detailed description.

DETAILED DESCRIPTION

[0008] This disclosure relates to a curable encapsulant composition for encapsulating electronic components. The curable encapsulant composition includes an epoxy resin composition, an aromatic dianhydride curing agent, optionally an additional curing promoter, and a curing catalyst. The inventors have discovered that an aromatic dianhydride, for example bisphenol-A dianhydride (BPA-DA), can be a useful curing agent for making high heat cured epoxy resins, and in particular when the aromatic dianhydride is soluble in the epoxy resin composition of the curable encapsulant composition. The curable encapsulant composition including the aromatic dianhydride as an epoxy curing agent can provide a cured thermoset product, for example an encapsulant for an electronic component, having good high heat resistance properties, such as a glass transition temperature of 230°C or greater.

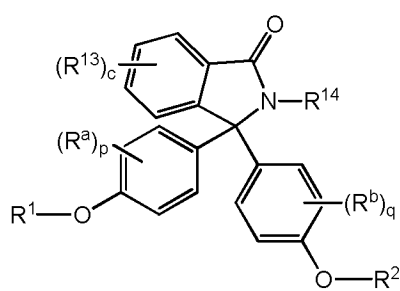
[0009] Provided herein is an electronic device encapsulated by a curable encapsulant composition including an epoxy resin composition, an aromatic dianhydride curing agent, an additional curing promoter comprising a monoanhydride, and a curing catalyst. The curable encapsulant composition after curing has a glass transition temperature of greater than or equal to 120°C. In particular aspects, the aromatic dianhydride curing agent is soluble in the epoxy resin composition. In some aspects, the curable encapsulant composition is substantially free of monoanhydride.

[0010] The stoichiometric ratio between the aromatic dianhydride curing agent and the epoxy resin composition can be 0.1:1 to 2.0:1, preferably 0.4:1 to 1.2:1, more preferably 0.6:1 to 1:1. The stoichiometric ratio is the molar ratio of total anhydride functionalities to total epoxy functionalities in the curable encapsulant composition. For example, the molar ratio of total anhydride functionalities from the dianhydride curing agent, the monoanhydride additional curing promoter, and optional additional anhydride curing promoters to the total epoxy

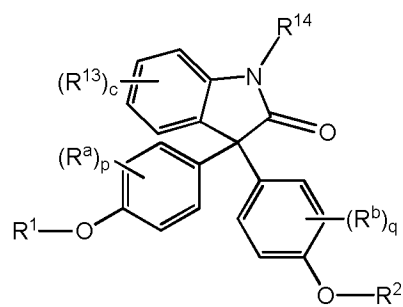
functionalities in the epoxy resin composition. The stoichiometric ratio is also referred to herein as the anhydride to epoxy (A/E) ratio.

[0011] The curable encapsulant composition includes 100 parts by weight of the epoxy resin composition, based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter. The epoxy resin composition can include one or more epoxy resins, such as bisphenol A epoxy resin, a triglycidyl-substituted epoxy resin, a tetraglycidyl-substituted epoxy resin, a bisphenol F epoxy resin, a phenol novolak epoxy resin, a cresol novolak epoxy resin, a cycloaliphatic diglycidyl ester epoxy resin, a cycloaliphatic epoxy resin comprising a ring epoxy group, an epoxy resin containing a spiro-ring, a hydantoin epoxy resin, or a combination thereof. In a particular aspect, the epoxy resin is bisphenol-A diglycidyl ether (BPA-DGE).

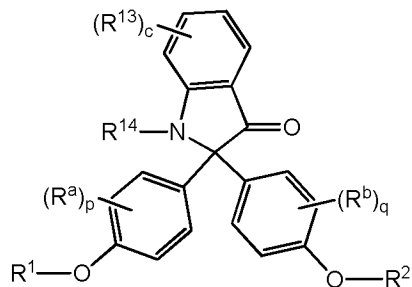
[0012] In some aspects, the epoxy resin composition may include one or more “high heat” epoxy compounds of formulas (I) to (IX):



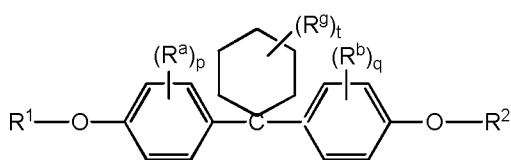
(I)



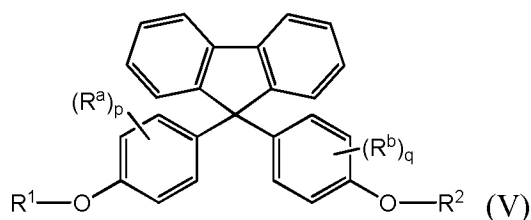
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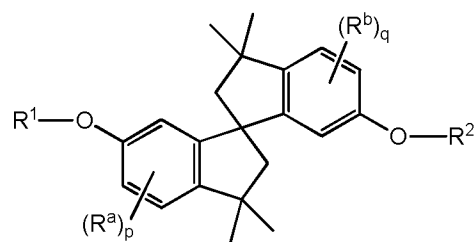
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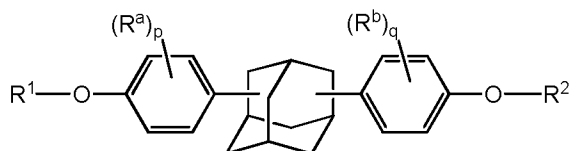
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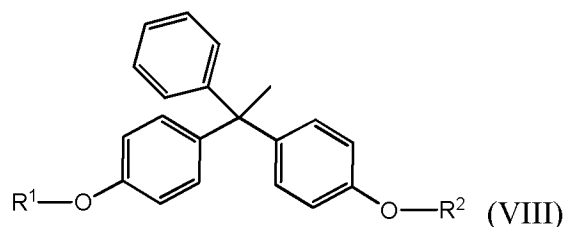
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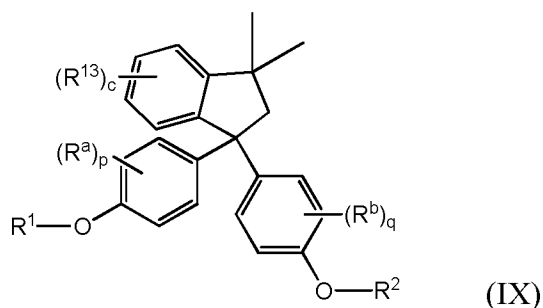
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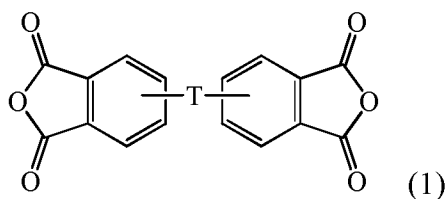


wherein, in Formulas (I) to (IX), R^1 and R^2 at each occurrence are each independently an epoxide-containing functional group; R^a and R^b at each occurrence are each independently halogen, C_{1-12} alkyl, C_{2-12} alkenyl, C_{3-8} cycloalkyl, or C_{1-12} alkoxy; p and q at each occurrence are each independently 0 to 4; R^{13} at each occurrence is independently a halogen or a C_{1-6} alkyl group; c at each occurrence is independently 0 to 4; R^{14} at each occurrence is independently a C_{1-6} alkyl, phenyl, or phenyl substituted with up to five halogens or C_{1-6} alkyl groups; R^g at each occurrence is independently C_{1-12} alkyl or halogen, or two R^g groups together with the carbon atoms to which they are attached form a four-, five, or six-membered cycloalkyl group; and t is 0 to 10.

[0013] In other aspects, the epoxy resin composition does not include a compound of formulas (I) to (IX). That is, the epoxy resin composition, and by extension the curable encapsulant composition, is free of the high heat epoxy compound of formulas (I) to (IX). Preferably, the epoxy resin composition does not include a compound of formulas (I) to (IX).

[0014] The curable encapsulant composition includes 2 to 200 parts by weight of the aromatic dianhydride curing agent, based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter. For example, the curable encapsulant composition can include 5 to 200 parts by weight, preferably 10 to 200 parts by weight, more preferably 10 to 180 parts by weight of the aromatic dianhydride curing agent, based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter.

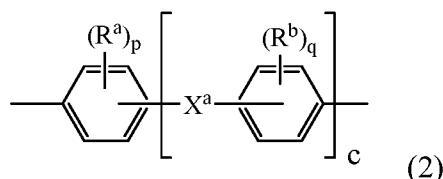
[0015] The aromatic dianhydride curing agent can be of the formula (1)



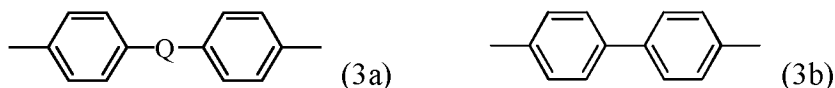
wherein T is $-O-$, $-S-$, $-C(O)-$, $-SO_2-$, $-SO-$, $-C_yH_{2y}-$ wherein y is an integer from 1 to 5 or a halogenated derivative thereof, or $-O-Z-O-$ wherein Z is an aromatic C_{6-24} monocyclic or polycyclic moiety optionally substituted with 1 to 6 C_{1-8} alkyl groups, 1 to 8 halogen atoms, or a

combination thereof. In some aspects, the R^1 is a monovalent C_{1-13} organic group. In some aspects, T is -O- or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions. In particular aspects, T is not -C(O)-. In particular aspects, T is not -O-, -C(O)-, -SO₂-, or -SO-. In another aspect, T is not -C(O)-.

[0016] Exemplary groups Z include groups of formula (2)



wherein R^a and R^b are each independently the same or different, and are a halogen atom or a monovalent C_{1-6} alkyl group, for example; p and q are each independently integers of 0 to 4; c is 0 to 4; and X^a is a bridging group connecting the hydroxy-substituted aromatic groups, where the bridging group and the hydroxy substituent of each C_6 arylene group are disposed ortho, meta, or para (specifically para) to each other on the C_6 arylene group. The bridging group X^a can be a single bond, -O-, -S-, -S(O)-, -S(O)₂-, -C(O)-, or a C_{1-18} organic bridging group. The C_{1-18} organic bridging group can be cyclic or acyclic, aromatic or non-aromatic, and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous. The C_{1-18} organic group can be disposed such that the C_6 arylene groups connected thereto are each connected to a common alkylidene carbon or to different carbons of the C_{1-18} organic bridging group. A specific example of a group Z is a divalent group of the formula (3a) or (3b)



wherein Q is -O-, -S-, -C(O)-, -SO₂-, -SO-, -P(R^a)(=O)- wherein R^a is a C_{1-8} alkyl or C_{6-12} aryl, or -C_yH_{2y}- wherein y is an integer from 1 to 5 or a halogenated derivative thereof (including a perfluoroalkylene group). In some aspects, Q is 2,2-isopropylidene. In some aspects, T is -O-Z-O-, preferably wherein Z is derived from bisphenol A (i.e., Z is 2,2-(4-phenylene)isopropylidene).

[0017] Illustrative examples of aromatic dianhydrides include 3,3-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride; 2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(2,3-

dicarboxyphenoxy)diphenyl sulfone dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl ether dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride; and 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride. In particular aspects, the aromatic dianhydride curing agent is bisphenol-A dianhydride.

[0018] In a particular aspect, the aromatic dianhydride curing agent does not include substituted or unsubstituted benzophenonetetracarboxylic acid dianhydride, substituted or unsubstituted oxydiphthalic acid dianhydride, substituted or unsubstituted 4,4'-(hexafluoroisopropylidene) diphthalic acid dianhydride, or a combination thereof.

[0019] The aromatic dianhydride curing agent can be soluble in the epoxy resin composition. The term “soluble in the epoxy resin composition” means that there is a temperature range where a combination of the aromatic dianhydride curing agent and the epoxy resin composition can be combined to form a homogeneous phase. As used herein, “forming a homogeneous phase” means creating a state where there is no visible separation between the components. The homogeneous phase can be formed in a certain temperature range without regard to any separation that may occur outside of that temperature range, for example, at room temperature. For example, a combination of the aromatic dianhydride curing agent and the epoxy resin composition can be stirred, heated, or heated under stirring to form a homogeneous phase.

[0020] In some aspects, the aromatic dianhydride curing agent can be soluble in the epoxy resin composition at a temperature from 50 to 200°C. For example, the aromatic dianhydride curing agent can be soluble in the epoxy resin composition from 80 to 200°C, more preferably from 100 to 190°C, even more preferably from 120 to 180°C.

[0021] The aromatic dianhydride curing agent can be soluble in the epoxy resin composition without the inclusion of any additives or solvents to improve the solubility of the dianhydride. In an aspect, the curable encapsulant composition is substantially free of solvent or solvents. In a particular aspect, the curable encapsulant composition is free of solvent. The term “substantially free of solvent” means that the curable encapsulant composition contains less than 500 parts per million (ppm) by weight of solvent. A “solvent free” curable encapsulant composition can have greater than 0 to 450 ppm by weight, preferably greater than 0 to 300 ppm by weight, more preferably greater than 0 to 200 ppm by weight, even more preferably greater

than 0 to 100 ppm by weight of solvent, based on the total weight of the curable encapsulant composition.

[0022] In an aspect, the curable encapsulant composition can include 0.1 to 5 weight percent (wt%) of a curing catalyst, based on the total weight of the composition. For example, the curable encapsulant composition can include 0.4 to 4 wt%, preferably 0.6 to 3 wt%, more preferably 0.7 to 2 wt% of the curing catalyst, based on the total weight of the composition.

[0023] The curing catalyst can be a heterocyclic curing catalyst. Heterocyclic compounds include benzotriazoles; triazines; piperazines such as aminoethylpiperazine, N-(3-aminopropyl)piperazine, or the like; imidazoles such as 1-methylimidazole, 2-methylimidazole, 3-methylimidazole, 4-methylimidazole, 5-methylimidazole, 1-ethylimidazole, 2-ethylimidazole, 3-ethylimidazole, 4-ethylimidazole, 5-ethylimidazole, 1-n-propylimidazole, 2-n-propylimidazole, 1-isopropylimidazole, 2-isopropylimidazole, 1-n-butylimidazole, 2-n-butylimidazole, 1-isobutylimidazole, 2-isobutylimidazole, 2-undecyl-1H-imidazole, 2-heptadecyl-1H-imidazole, 1,2-dimethylimidazole, 1,3-dimethylimidazole, 2,4-dimethylimidazole, 2-ethyl-4-methylimidazole, 1-phenylimidazole, 2-phenyl-1H-imidazole, 4-methyl-2-phenyl-1H-imidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-methylimidazole, 1-benzyl-2-phenylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, 1-cyanoethyl-2-phenyl-4,5-di(2-cyanoethoxy)methylimidazole; cyclic amidine such as 4-diazabicyclo(2,2,2)octane (DABCO), diazabicycloundecene (DBU), 2-phenyl imidazoline, or the like; N,N-dimethylaminopyridine (DMAP); sulfamidate; or a combination thereof. In a particular embodiment, the curable encapsulant composition does not include a heterocyclic curing catalyst.

[0024] The curable encapsulant composition further includes an additional curing promoter comprising a monoanhydride. The term “curing promoter” as used herein encompasses compounds whose roles in curing epoxy resins are variously described as those of a hardener, a hardening accelerator, a curing catalyst, and a curing co-catalyst, among others.

[0025] Exemplary monoanhydrides include, but are not limited to, maleic anhydride (MA), phthalic anhydride (PA), hexahydro-*o*-phthalic anhydride (HEPA), tetrahydrophthalic anhydride (THPA), methyltetrahydrophthalic anhydride (MTHPA), methylhexahydrophthalic anhydride (MHHPA), nadic methyl anhydride (methyl himic anhydride, MHA), tetrachlorophthalic anhydride (TCPA), trimellitic anhydride (TMA), or the like, or a combination thereof. Preferably, the monoanhydride curing promoter includes MTHPA.

[0026] The composition can further include other additional curing promoters in addition to the monoanhydride. Other exemplary additional curing promoters include, for example, amines, dicyandiamide, polyamides, amidoamines, Mannich bases, other anhydrides, phenol-formaldehyde resins, carboxylic acid functional polyesters, polysulfides, polymercaptans, isocyanates, cyanate esters, and combinations thereof.

[0027] In some aspects, the additional curing promoter further includes an amine. The amine can be a polyamine, a tertiary amine, an amidine, and combinations thereof. Examples of suitable polyamines include amine hardeners such as isophoronediamine, triethylenetetraamine, diethylenetriamine, aminoethylpiperazine, 1,2- and 1,3-diaminopropane, 2,2-dimethylpropylenediamine, 1,4-diaminobutane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane, 1,12-diaminododecane, 4-azaheptamethylenediamine, N,N'-bis(3-aminopropyl)butane-1,4-diamine, cyclohexanediamine, 4,4'-methylenedianiline, diethyltoluenediamine, *m*-phenylenediamine, *p*-phenylenediamine, tetraethylenepentamine, 3-diethylaminopropylamine, 3,3'-iminobispropylamine, 2,4-bis(*p*-aminobenzyl)aniline, tetraethylenepentamine, 3-diethylaminopropylamine, 2,2,4- and 2,4,4-trimethylhexamethylenediamine, 1,2- and 1,3-diaminocyclohexane, 1,4-diamino-3,6-diethylcyclohexane, 1,2-diamino-4-ethylcyclohexane, 1,4-diamino-3,6-diethylcyclohexane, 1-cyclohexyl-3,4-diaminocyclohexane, 4,4'-diaminodicyclohexylmethane, 4,4'-diaminodicyclohexylpropane, 2,2-bis(4-aminocyclohexyl)propane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 3-amino-1-cyclohexaneaminopropane, 1,3- and 1,4-bis(aminomethyl)cyclohexane, *m*- and *p*-xylylenediamine, diethyl toluene diamines, and combinations thereof. In some aspects, the curing promoter comprises a hardener selected from the group consisting of *m*-phenylenediamine, 4,4'-diaminodiphenylmethane, or a combination thereof.

[0028] Examples of amine compounds further include tertiary amine hardening accelerators such as triethylamine, tributylamine, dimethylaniline, diethylaniline, benzyldimethylamine (BDMA) α -methylbenzyldimethylamine, N,N-dimethylaminoethanol, N,N-dimethylaminocresol, tri(N,N-dimethylaminomethyl)phenol, and combinations thereof. Examples of suitable amine compounds further include imidazole hardening accelerators such as 2-methylimidazole, 2-ethylimidazole, 2-laurylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, 4-methylimidazole, 4-ethylimidazole, 4-laurylimidazole, 4-heptadecylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4-hydroxymethylimidazole, 2-ethyl-4-methylimidazole, 2-ethyl-4-hydroxymethylimidazole, 1-cyanoethyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, and combinations thereof. Examples

of suitable amine compounds further include cyclic amidine hardening accelerators such as 4-diazabicyclo(2,2,2)octane (DABCO), diazabicycloundecene (DBU), 2-phenyl imidazoline, or a combination thereof.

[0029] The additional curing promoter can include other amine compounds. Examples of other amine compounds include hardeners such as ketimines, which are the reaction products of ketones and primary aliphatic amines; polyetheramines, which are the reaction products of polyols derived from ethylene oxide or propylene oxide with amines; amine-terminated polyamides, prepared by the reaction of dimerized and trimerized vegetable oil fatty acids with polyamines; amidoamines, imidazolines, and combinations thereof, for example the reaction product of diethylene triamine and tall-oil fatty acid.

[0030] The additional curing promoter can further comprise a phenol-formaldehyde resin. Exemplary phenol-formaldehyde resins include, for example, novolac type phenol resins, resole type phenol resins, aralkyl type phenol resins, dicyclopentadiene type phenol resins, terpene modified phenol resins, biphenyl type phenol resins, bisphenol type phenol resins, triphenylmethane type phenol resins, or a combination thereof.

[0031] The additional curing promoter can further comprise a Mannich base. Examples of Mannich bases are the reaction products of an amine with phenol and formaldehyde, melamine-formaldehyde resins, urea-formaldehyde resins, or a combination thereof.

[0032] In addition to the tertiary amines listed above, the additional curing promoter can comprise other hardening accelerators. Examples of other hardening accelerators are substituted ureas, for example 3-phenyl-1,1-dimethyl urea; the reaction product of phenyl isocyanate with dimethylamine; the reaction product of toluene diisocyanate with dimethylamine; quaternary phosphonium salts, such as tetraalkyl and alkyltriphenylphosphonium halide; or a combination thereof.

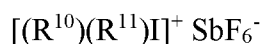
[0033] The additional curing promoter can comprise a metal salt, for example a copper (II) or aluminum (III) salt of an aliphatic or aromatic carboxylic acid. Exemplary metal salts include the copper (II), tin (II), and aluminum (III) salts of acetate, stearate, gluconate, citrate, benzoate, and like anions, or a combination thereof. The additional curing promoter can comprise a copper (II) or aluminum (III) β -diketonate. Exemplary metal diketonates include the copper (II) and aluminum (III) salts of acetylacetonate. The additional curing promoter can comprise a borontrifluoride-trialkylamine complex. An illustrative boron trifluoride-trialkylamine complex is boron trifluoride-trimethylamine complex.

[0034] The additional curing promoter can comprise a latent cationic cure catalyst. Latent cationic cure catalysts are used, for example, in UV-cured epoxy resin compositions.

Latent cationic cure catalysts include, for example, diaryliodonium salts, phosphonic acid esters, sulfonic acid esters, carboxylic acid esters, phosphonic ylides, triarylsulfonium salts, benzyliodonium salts, aryldiazonium salts, benzylpyridinium salts, benzylammonium salts, isoxazolium salts, or a combination thereof. For example, the additional curing promoter can be a latent cationic cure catalyst comprising a diaryliodonium salt having the structure



wherein R^{10} and R^{11} are each independently a C_6 - C_{14} monovalent aromatic hydrocarbon radical, optionally substituted with from 1 to 4 monovalent radicals selected from C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, nitro, and chloro; and wherein X^- is an anion. In some aspects, the curing promoter is a latent cationic cure catalyst comprising a diaryliodonium salt having the structure



wherein R^{10} and R^{11} are each independently a C_6 - C_{14} monovalent aromatic hydrocarbon radical, optionally substituted with from 1 to 4 monovalent radicals selected from C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, nitro, and chloro. In some aspects, the curing promoter is a latent cationic cure catalyst comprising 4-octyloxyphenyl phenyl iodonium hexafluoroantimonate. In particular aspects, the curable encapsulant composition does not include a latent cationic cure catalyst.

[0035] When used, the amount of additional curing promoter will depend on the type of curing promoter, as well as the identities and amounts of the other components of the curable encapsulant composition. For example, the additional curing promoter can be present in an amount of 10 to 100 parts by weight, preferably 20 to 100 parts by weight, more preferably 20 to 80 parts by weight, based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter.

[0036] In some aspects, the curable encapsulant composition is substantially free of a monoanhydride curing promoter and/or a monoanhydride. The term “substantially free of monoanhydride” means that the curable encapsulant composition contains less than 500 parts per million (ppm) by weight of monoanhydride. For example, a “monoanhydride free” curable encapsulant composition can have less than 450 ppm by weight, preferably less than 300 ppm by weight, more preferably less than 200 ppm by weight, even more preferably less than 100 ppm by weight of monoanhydride, based on the total weight of the curable encapsulant composition.

[0037] The curable encapsulant composition can include an inorganic filler. Exemplary inorganic fillers include, for example, alumina, silica (including fused silica, fumed silica, colloidal silica, and crystalline silica), boron nitride (including spherical boron nitride), aluminum nitride, silicon nitride, titania, titanium dioxide, titanium diboride, magnesia, magnesium oxide, magnesium silicate, glass fibers (chopped, milled and cloth), glass bubbles,

hollow glass microsphere, aramid fibers, glass mat, talc, fly ash, kaolin, clay (aluminum silicate), antimony trioxide, calcium carbonate, calcium oxide, carbon black, zinc oxide, or a combination thereof. Exemplary glass fibers include those based on E, A, C, ECR, R, S, D, and NE glasses, as well as quartz.

[0038] The inorganic filler can be treated with a silane coupling agent. Exemplary silane coupling agents include, but are not limited to, aminosilanes, epoxysilanes, mercaptosilanes, styrylsilanes, or a combination thereof. Exemplary aminosilanes include (4-aminobutyl)-dimethylmethoxysilane, N-(2-aminoethyl-3-aminopropyl)-methyldimethoxysilane, N-(2-aminoethyl-3-aminopropyl)trimethoxysilane, (3-aminopropyl)-methyldiethoxysilane, (3-aminopropyl)-triethoxysilane, (3-aminopropyl)-trimethoxysilane, 3-(N-aminophenyl)-propyltrimethoxysilane, or the like. Exemplary epoxysilanes include 2-(3,4-epoxy cyclohexyl-ethyl)-trimethoxysilane, (3-glycidoxy propyl)- bis(trimethylsiloxy)-methylsilane, (3-glycidoxypropyl)-diisopropylethoxysilane, (3-glycidoxypropyl)-dimethylethoxysilane, (3-glycidoxypropyl)-methyldiethoxysilane, (3-glycidoxypropyl)-methyldiisopropenoxysilane, (3-glycidoxypropyl)-trimethoxysilane, or the like. Exemplary mercaptosilanes include (3-mercaptopropyl)-methyldimethoxysilane, (3-mercaptopropyl)-trimethoxysilane, (mercaptopmethyl)-dimethylethoxysilane, (mercaptopmethyl)-methyldiethoxysilane, (3-mercaptopropyl)-triethoxysilane, or the like. Exemplary styrylsilanes include styrylethyltrimethoxysilane, 3-(N-styrylmethyl-2-aminoethylamino)-propyltrimethoxysilane, or the like.

[0039] The treatment with the silane coupling agent can increase compatibility of the otherwise hydrophilic inorganic filler with an at least partially non-polar organic phase matrix. In the case of silica, the treatment can leave residual active termination sites on the silica (e.g., silanol) that can reduce stability. Therefore, a subsequent or second treatment of the silica can be performed with a capping or passivating agent. Exemplary passivating agents include a silazane, such as hexamethyldisilazane. This two-part treatment can remove substantially all of the active termination sites available on the silica that could reduce stability or shelf life, or undesirably increase viscosity or initiate crosslinking over time.

[0040] The inorganic filler can include particles having one or more morphologies and physical dimensions. For example, the inorganic filler can include one or more of spherical particles, semi-spherical particles, spheroids, oblates, amorphous particles, hollow spheres, porous materials, rods, whiskers, geometric shapes, tubes, fibers having at least one dimension that is longer than another dimension, or the like. The inorganic filler can have a mean or average dimension distribution that is less than or equal to 75 micrometers (μm), less than or

equal to 50 μm , less than or equal to 35 μm , less than or equal to 25 μm , or the dimension can be sub-micrometer. The inorganic filler can include particles having a bimodal particle size distribution, a trimodal particle size distribution, or a higher modality particle size distribution. In particular aspects, the inorganic filler includes particles having a bimodal particle size distribution and substantially all of the particles present are spherical.

[0041] The inorganic filler can include colloidal silica having an average particle diameter of less than 5 nanometers (nm), or in a range of from 5 to 10 nm, 10 to 20 nm, 20 to 40 nm, or 40 to 500 nm. The colloidal silica can be spherical, semi-spherical, amorphous, or geometric shaped.

[0042] When an inorganic filler is utilized, the curable encapsulant composition can include from 1 to 40 wt%, from 40 to 60 wt%, from 60 to 86 wt%, or from 86 to 92 wt% of the inorganic filler, based on the total weight of the curable encapsulant composition.

[0043] In some aspects, the curable encapsulant composition includes an additive composition. The additive composition can include a particulate filler, a fibrous filler, a reinforcing material, an antioxidant, a heat stabilizer, a light stabilizer, a ultraviolet light stabilizer, a ultraviolet light-absorbing compound, a near infrared light-absorbing compound, an infrared light-absorbing compound, a plasticizer, a lubricant, a release agent, a antistatic agent, an anti-fog agent, an antimicrobial agent, a colorant, a surface effect additive, a radiation stabilizer, a flame retardant, flame retardant synergists such as antimony pentoxide, an anti-drip agent, a fragrance, an adhesion promoter, a flow enhancer, a coating additive, a polymer different from the thermoset (epoxy resin) polymer, or a combination thereof. In a preferred aspect, the curable encapsulant composition is substantially free of any polymer other than the thermoset (epoxy resin) polymer.

[0044] Other optional additives can be included in the curable encapsulation composition. Exemplary other additives include one or more of a functionalized liquid rubber, micronized rubber, metal adhesion promoter, soldermask adhesion promoter, ion exchange additive, antioxidant, or the like.

[0045] The curable encapsulation composition can be manufactured by combining the epoxy resin composition, the aromatic dianhydride curing agent, the curing catalyst, and optionally the additional curing promoter at a temperature of 100 to 200°C, preferably 120 to 190°C, more preferably 130 to 180°C to provide the curable encapsulant composition.

[0046] In some aspects, the curable encapsulant composition and/or reaction mixture contains no solvent or reactive diluent. In other aspects, the curable encapsulant composition

and/or the reaction mixture further includes a solvent with the proviso that the solvent does not render an otherwise insoluble aromatic dianhydride soluble in the epoxy resin composition.

[0047] For example, the solvent can be C₃₋₈ ketones, C₄₋₈ *N,N*-dialkylamides, C₄₋₁₆ dialkyl ethers, C₆₋₁₂ aromatic hydrocarbons, C₃₋₆ alkyl alkanoates, C₂₋₆ alkyl nitriles, C₂₋₆ dialkyl sulfoxides, or a combination thereof. Examples of C₃₋₈ ketones include acetone, methyl ethyl ketone, methyl isobutyl ketone, and combinations thereof. Examples of C₄₋₈ *N,N*-dialkylamides include dimethylformamide, dimethylacetamide, *N*-methyl-2-pyrrolidone, and combinations thereof. Examples of C₄₋₁₆ dialkyl ethers include tetrahydrofuran, dioxane, and combinations thereof. The C₄₋₁₆ dialkyl ether can optionally further include one or more ether oxygen atoms within the alkyl groups and one or more hydroxy substituents on the alkyl groups, for example the C₄₋₁₆ dialkyl ether can be ethylene glycol monomethyl ether. The aromatic hydrocarbon solvent can be an ethylenically unsaturated solvent. Examples of C₆₋₁₂ aromatic hydrocarbons include benzene, toluene, xylenes, styrene, divinylbenzenes, and combinations thereof. Examples of C₃₋₆ alkyl alkanoates include methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, and combinations thereof. Examples of C₂₋₆ alkyl cyanides include acetonitrile, propionitrile, butyronitrile, and combinations thereof. Examples of C₂₋₆ dialkyl sulfoxides include dimethyl sulfoxide, methyl ethyl sulfoxide, diethyl sulfoxide, and combinations thereof. In some aspects, the solvent comprises acetone, methyl ethyl ketone, *N*-methyl-2-pyrrolidone, toluene, or a combination thereof. In still other aspects, the solvent can be a halogenated solvent such as methylene chloride, chloroform, 1,1,1-trichloroethane, chlorobenzene, or the like.

[0048] In an aspect, the electronic device is encapsulated by the curable encapsulant composition include: 100 parts by weight of an epoxy resin composition comprising a bisphenol A epoxy resin; 30 to 200 parts by weight of an aromatic dianhydride curing agent comprising a bisphenol-A dianhydride; an effective amount of a curing catalyst; and an additional curing promoter comprising methyltetrahydrophthalic anhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, and wherein the curable encapsulant composition after curing has a glass transition temperature of 160 to 320°C, as determined by DMA.

[0049] In an aspect, the electronic device is encapsulated by the curable encapsulant composition include: 100 parts by weight of an epoxy resin composition comprising a bisphenol A epoxy resin; 30 to 200 parts by weight of an aromatic dianhydride curing agent comprising a bisphenol-A dianhydride; an effective amount of a curing catalyst; and an additional curing promoter comprising methyltetrahydrophthalic anhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and

the additional curing promoter, and further comprising an inorganic filler, carbon black, a silane coupling agent, and a lubricant, wherein the curable encapsulant composition after curing has a glass transition temperature of 160 to 320°C, as determined by DMA.

[0050] In an aspect, the electronic device is encapsulated by the curable encapsulant composition include: 100 parts by weight of an epoxy resin composition comprising a bisphenol A epoxy resin; 30 to 200 parts by weight of an aromatic dianhydride curing agent comprising a bisphenol-A dianhydride; an effective amount of a curing catalyst; and an additional curing promoter comprising methyltetrahydrophthalic anhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, and further comprising silicon dioxide and carbon black, wherein the curable encapsulant composition after curing has a glass transition temperature of 160 to 220°C, as determined by DMA.

[0051] Also provided is a method encapsulating an electronic or optical device with the curable encapsulation composition. The method can include heating the curable encapsulation composition at a temperature sufficient to soften or liquefy the mixture, for example to melt the composition, and subsequently encapsulating at least a portion of the electronic or optical device. For example, the encapsulating can be by flowing a molten, softened, or liquefied portion into contact with the electronic or optical device. The encapsulated electronic or optical device can then be cured.

[0052] The curable encapsulant compositions can be employed in a transfer molding process. In some aspects, the curable encapsulant composition can be formed into a pellet. Pellets can be used in a transfer molding process, for example, as the encapsulant of an electronic device such as a circuit. Pellets can be readily formed by conventional techniques such as compression of the curable encapsulant composition in a mold at ambient temperature.

[0053] The transfer molding apparatus can include a pot, which can be a cylindrical cavity fitted with a retractable plunger. The curable encapsulant composition in pellet form and the pot can have approximately the same diameter. The pot can be kept hot, at the same temperature as the molding tool. After the pellet has been inserted into the pot, the plunger presses the pellet through an opening at the bottom of the pot into the hot runner system of the molding tool. Cycle time can be in a range of 1 to 4 minutes.

[0054] The pot and the molding tool can be independently held at temperatures that are greater than 50°C, for example from 50 to 175°C, from 100 to 175°C, from 130 to 175°C, from 140 to 175°C, or greater than 175°C. Temperatures higher than 150°C can be useful with, for example, lead-free solder applications.

[0055] Pellets under 7 grams (g) can be softened within a few seconds by inserting the pellet into the transfer pot. Larger pellets (over 7 g) can be pre-heated, for example, using a radio frequency pre-heater with an infrared pyrometer, and then inserted into the transfer pot.

[0056] A low softening temperature for the pellet can inhibit the curable encapsulant composition from flowing out of the pot before the pellet has softened. For example, the pellet can deform or sinter to other pellets. The softened pellets can glom to each other, and/or the sides of the container, and not pour as free-flowing pellets. A softening temperature too high can undesirably cure the pellets prior to use.

[0057] Transfer-molding suitability can correlate to a spiral flow length. Spiral flow length can be measured by SEMI G11-88 recommended practice for ram follower gel time, and for spiral flow of thermal setting molding compounds, or by EMMI 1-66. Spiral flow length can be measured at 1 MPa and 150°C. The spiral flow length can be controlled by selection of, for example, reactive diluent type, and amount. Alternatively or additionally, the spiral flow length can be increased by the presence of a polymerization inhibitor, and may be decreased by the presence of filler, colorant, and/or flame retardant.

[0058] The curable encapsulant composition can be cured, for example, following the initial encapsulation of an electronic or optical device. There is no particular limitation on the method by which the composition can be cured, with the proviso that the curing does not damage or adversely affect the underling device. The curable encapsulant composition can, for example, be cured thermally or by using irradiation techniques, including UV irradiation and electron beam irradiation. When heat curing is used, the temperature selected can be 80 to 300°C, and preferably 120 to 250°C. The heating period can be 1 minute to 10 hours, though such heating period may advantageously be 1 minute to 6 hours, preferably 2 minutes to 4 hours, more preferably 15 minutes to 4 hours. Such curing may be staged to produce a partially cured and often tack-free resin, which then is fully cured by heating for longer periods or temperatures within the aforementioned ranges.

[0059] The cured product of the curable encapsulant composition has a glass transition temperature (T_g) of greater than or equal to 120°C, preferably greater than or equal to 160°C, more preferably greater than or equal to 180°C, even more preferably greater than or equal to 200°C, still more preferably greater than or equal to 250 °C.

[0060] The cured product of the curable encapsulant composition can have a hardness of from 20 to 200 Shore D, preferably from 30 to 160 Shore D, more preferably from 50 to 150 Shore D, as measured according to ASTM D2240

[0061] The cured product of the curable encapsulant composition can have a flex strength of from 65 to 200 megapascals (MPa), preferably from 70 MPa to 160 MPa, more preferably from 75 to 150 MPa, as measured according to ASTM D790.

[0062] Also provided is an electronic device comprising the cured product of the curable encapsulant composition. The electronic device can include a substrate comprising any materials commonly used in the electronics industry, including, but not limited to, polymer, glass, metal, ceramic, or the like, and can be flexible or rigid. The substrate can be a printed circuit board, an epoxy circuit card, or a copper lead frame. The substrate can be a carrier for a metallization pattern which can include an interconnection pad and a mounting area on which an electronic component can be mounted, for instance, by an adhesive. The electronic component can be soldered to the mounting area.

[0063] Representative electronic components that can be encapsulated include one or more transistors, capacitors, relays, diodes, resistors, networks of resistors, integrated circuits, or the like. The electronic component can be connected with the wires to various other electronic components, such as interconnection pads. The wires can be metal wires, such as copper, gold, aluminum, or the like.

[0064] The electronic component and the wires are at least partially encapsulated with the cured product of the curable encapsulant composition. The thickness of the cured encapsulant product can be from 0.1 to 3.5 mm, preferably from 0.5 to 3.5 mm, more preferably from 1 to 3 mm.

[0065] The curable encapsulant composition can be applied by transfer molding, as described above. The substrate with the electronic component can be placed in a transfer molding machine having a mold. The curable encapsulant composition can be preheated and inserted into a pot, and then forced from a pot into the hot mold cavity. The curable encapsulant composition can flow and mold around the electronic component and the associated wires, and around at least portions of the interconnect pads, the mounting areas, and the substrate. Upon solidification, the molded part may be ejected from the mold. The curing can be performed in the mold or after ejection from the mold.

[0066] This disclosure is further illustrated by the following examples, which are non-limiting.

EXAMPLES

[0067] Materials used in the examples are described in Table 1.
Table 1.

Component	Description	Source
BPA-DGE	Bisphenol A diglycidyl ether, epoxy equivalent weight (EEW) of 405 grams per equivalent (g/eq), CAS Reg. No. 1675-54-3, obtained as DER 332	Sigma-Aldrich
MTHPA	Methyltetrahydrophthalic anhydride, EEW of 166.2, CAS Reg. No. 11070-44-3	TCI
BPADA	Bisphenol-A dianhydride, EEW of 260.25 g/eq, CAS Reg. No. 38103-06-9	SABIC
2,4-EMI	2-Ethyl-4-methylimidazole, CAS Reg. No. 931-36-2	Sigma-Aldrich

[0068] Glass transition temperature (T_g) was measured on a RDA III dynamic mechanical analyzer from TA Instruments. Samples (40 mm × 4 mm × 3 mm) were heated in the range of -100°C to 300°C at a heating rate of 5 °C/min and a frequency of 1 Hertz (Hz). T_g was determined as the temperature of the tan δ maximum.

Example 1

[0069] Examples 1-1 to 1-15 are prophetic examples of and can be prepared as follows. The diglycidyl ether compound(s) and anhydride curing agent(s) are combined in a universal agitator. The resultant combination is mixed at 150°C for 20 minutes. Thereafter, the temperature of the mixture is lowered to 80°C, the inorganic filler is added thereto, and the combination is stirred at 80°C for 20 minutes. The temperature is reduced to 70°C and the curing catalyst (2,4-EMI) is added thereto. This mixture is homogenized by stirring at 70°C for 2 minutes to ensure mixing of all the components, and then cooled to room temperature (ca. 23°C).

[0070] Comparative Examples C-1 to C-4 are prophetic comparative examples and can be prepared in the same manner, but do not include BPADA as a curing agent.

[0071] The prophetic curable encapsulant compositions are provided in Tables 2 and 3, where the amounts are in parts by weight (pbw) unless otherwise indicated.

Table 2.

Component (pbw)	C-1	1-1	1-2	1-3	C-2	1-4	1-5	1-6
BPA-DGE	100	100	100	100	-	-	-	-
BF-DGE	-	-	-	-	100	100	100	100
TMB-DGE	-	-	-	-	-	-	-	-
PB-DGE	-	-	-	-	-	-	-	-
MTHPA	78.3	70.3	62.4	54.7	84.2	75.8	67.4	58.9
BPADA	-	12.2	24.5	36.7	-	13.2	26.4	39.5
Molar Ratio (A/E)	1.4	1.5	1.5	1.5	1.5	1.5	1.6	1.6
2,4-EMI (wt%)	1.8	1.8	1.9	1.9	1.8	1.9	1.9	2.0
Inorganic Filler	160.4	164.2	168.2	172.1	165.7	170.1	174.4	178.6
Carbon Black	3.6	3.6	3.7	3.8	3.7	3.8	3.9	4.0
Silane Coupling agent	2.7	2.7	2.8	2.9	2.8	2.8	2.9	3.0
Lubricant	2.1	2.2	2.2	2.3	2.2	2.3	2.3	2.4

Table 3.

Components	C-3	1-7	1-8	1-9	C-4	1-10	1-11	1-12	1-13	1-14	1-15
BPA-DGE	-	-	-	-	-	-	-	-	100	100	100
BF-DGE	-	-	-	-	-	-	-	-	-	106.6	-
TMB-DGE	-	-	-	-	100	100	100	100	-	-	-
PB-DGE	100	100	100	100	-	-	-	-	41.5	-	-
MTHPA	76.4	68.7	61.1	53.4	70.1	63.0	56.0	48.9	73.5	73.4	-
BPADA	-	11.9	23.9	36.0	-	11.0	21.9	32.9	49.2	49.3	122.2
A/E ratio	1.4	1.4	1.5	1.5	1.4	1.4	1.4	1.5	2.1	2.6	1.8
2,4-EMI (wt%)	1.8	1.8	1.9	1.9	1.7	1.7	1.8	1.8	2.6	3.3	2.2
Inorganic Filler	158.7	162.7	166.7	170.5	153.1	156.5	160.1	163.6	238.1	296.1	200
Carbon Black	3.5	3.6	3.7	3.8	3.4	3.5	3.6	3.6	5.3	6.6	4.4
Silane Coupling agent	2.6	2.7	2.8	2.8	2.6	2.6	2.7	2.7	4.0	4.9	3.3
Lubricant	2.1	2.2	2.2	2.3	2.0	2.1	2.1	2.2	3.2	3.9	2.7

Example 2

[0072] Examples 2-1 to 2-3 were prepared as follows. BPA-DGE, MTHPA, and BPADA were combined. The composition is mixed well at 23°C and heated at 125°C for 3 minutes to afford a homogenous mixture. The mixture was then cooled to 23°C and 2,4-EMI was added thereto. The resulting combination was heated at 110°C for 3 minutes and then poured into a preheated mold (135°C) and cured in the mold at 80°C for 30 minutes, 120°C for 30 minutes, 150°C for 30 minutes, and 180°C for 60 minutes to afford a rigid and clear casting.

[0073] Examples 2-4 to 2-8 were prepared as follows. BPA-DGE is heated at 160°C and combined with BPADA. A homogenous and transparent reaction mixture is afforded. The reaction mixture was cooled to 90°C and 2,4-EMI was added while stirring. The resulting mixture was poured into a preheated mold (130 °C) and then cured in the mold at 220°C for 60 minutes to afford a rigid and clear casting.

Comparative Example C-5

[0074] Comparative Example C-5 was prepared as follows. BPA-DGE and MTHPA were combined at 23°C with mixing. 2,4-EMI was then added to the mixture, the resulting combination was heated at 90°C, and then poured into a preheated mold (130°C). Curing was performed in the mold at 80°C for 30 minutes, 120°C for 30 minutes, 150°C for 30 minutes, and 180°C for 60 minutes to provide a rigid and clear casting.

[0075] The compositions and properties of Examples 2-1 to 2-8 and Comparative Example C-5 are provided in Table 4, where the amounts are in parts per hundred (phr) unless otherwise noted.

Table 4.

Example	BPA-DGE	MTHPA	BPADA	2,4-EMI (wt%)	A/E Ratio	Tg (°C)
C-5	100	78.1	-	1.8	0.8	145

2-1	100	70.3	12.2	1.8	0.8	164
2-2	100	62.5	24.5	1.9	0.8	173
2-3	100	54.7	36.7	1.9	0.8	182
2-4	100	-	61.2	1.6	0.4	233
2-5	100	-	91.7	1.9	0.6	246
2-6	100	-	122.3	2.2	0.8	264
2-7	100	-	152.9	2.5	1.1	251
2-8	100	-	168.2	2.7	1.2	231

[0076] As shown in Table 4, the T_g was found to increase with an increase in the amount of BPADA in Examples 2-1 to 2-3. Examples 2-4 to 2-8 show that BPADA can be used as the sole anhydride curing agent to achieve a T_g of greater than 230°C in cured compositions derived from BPA-DGE, which is surprising in view of the properties of cured compositions derived from other liquid epoxy resins. The optimum heat resistance was observed at A/E ratio of 0.8, as higher loadings of BPADA were unexpectedly found to decrease the T_g . The data indicate that BPADA can be used effectively as a curing or co-curing agent to prepare high heat resin formulations for use in applications such as semiconductor encapsulation.

[0077] This disclosure further encompasses the following aspects.

[0078] Aspect 1. An electronic device encapsulated by a curable encapsulant composition, the curable encapsulant composition comprising: 100 parts by weight of an epoxy resin composition; 30 to 200 parts by weight of an aromatic dianhydride curing agent; an effective amount of a curing catalyst; and an additional curing promoter comprising a monoanhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, and wherein the curable encapsulant composition after curing has a glass transition temperature of 120 to 320°C, preferably 160 to 320°C, more preferably 180 to 320°C, even more preferably 200 to 320°C, still more preferably 250 to 320°C, as determined by DMA.

[0079] Aspect 1a. An electronic device encapsulated by a curable encapsulant composition, the curable encapsulant composition comprising: 100 parts by weight of an epoxy resin composition; 30 to 200 parts by weight of an aromatic dianhydride curing agent; an effective amount of a curing catalyst; and an additional curing promoter comprising a monoanhydride; wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, wherein the curable encapsulant composition after curing has a glass transition temperature of 120 to 320°C, preferably 160 to 320°C, more preferably 180 to 320°C, even more preferably 200 to 320°C, still more preferably 250 to 320°C, as determined by DMA, and wherein the epoxy resin composition does not include a high heat epoxy compound of formulas (I) to (IX) as provided herein

[0080] Aspect 2. The electronic device of aspect 1, wherein the curable encapsulant composition comprises an anhydride to epoxy stoichiometric ratio (A/E) of 0.1:1 to 2.0:1, as determined by molar ratio of total anhydride functionalities to total epoxy functionalities in the curable encapsulant composition.

[0081] Aspect 3. The electronic device of any one or more of the preceding aspects, wherein the epoxy resin composition comprises an epoxy resin that is a bisphenol A epoxy resin, a triglycidyl-substituted epoxy resin, a tetraglycidyl-substituted epoxy resin, a bisphenol F epoxy resin, a phenol novolak epoxy resin, a cresol novolak epoxy resin, a cycloaliphatic diglycidyl ester epoxy resin, a cycloaliphatic epoxy resin comprising a ring epoxy group, an epoxy resin containing a spiro-ring, a hydantoin epoxy resin, or a combination thereof; preferably wherein the epoxy resin composition comprises bisphenol-A diglycidyl ether.

[0082] Aspect 4. The electronic device of any one or more of the preceding aspects, wherein the aromatic dianhydride curing agent has the formula (1) as provided herein; preferably wherein T is -O- or a group of the formula -O-Z-O- wherein Z is of the formula (2) as provided herein; more preferably wherein T is a group of the formula -O-Z-O- wherein Z is a divalent group of formulas (3a) or (3b) as provided herein; even more preferably wherein the aromatic dianhydride curing agent comprises bisphenol-A dianhydride.

[0083] Aspect 5. The electronic device of any one of the preceding aspects, wherein the additional curing promoter further comprises an amine, a dicyandiamide, a polyamide, an amidoamine, a Mannich base, a phenol-formaldehyde resin, a carboxylic acid functional polyester, a polysulfide, a polymercaptan, an isocyanate, a cyanate ester, or a combination thereof; preferably wherein the monoanhydride is benzophenone tetracarboxylic anhydride, (C₁₋₆ alkyl)styrene-maleic anhydride copolymer, chlorendic anhydride, dodecenyl succinic anhydride, hexahydrophthalic anhydride, hexahydro-4-methylphthalic anhydride, maleic anhydride, methylbutenyl tetrahydrophthalic anhydride, methylcyclohexene dicarboxylic anhydride, methyl nadic anhydride, methyltetrahydrophthalic anhydride, nadic anhydride, phthalic anhydride, pyromellitic anhydride, succinic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, or a combination thereof.

[0084] Aspect 6. The electronic device of any one or more of the preceding aspects, wherein the curing catalyst comprises a substituted or unsubstituted C₃₋₆ heterocycle comprising 1 to 4 ring heteroatoms, wherein each heteroatom is independently the same or different, and is nitrogen, oxygen, phosphorus, silicon, or sulfur; preferably wherein the curing catalyst comprises a C₃₋₄ five-membered ring wherein the ring heteroatoms are one or two nitrogen atoms.

[0085] Aspect 7. The electronic device of any one or more of the preceding aspects, further comprising an inorganic filler, preferably wherein the inorganic filler is fused silica, fumed silica, colloidal silica, aluminum oxide, boron nitride, titanium dioxide, titanium diboride, talc, fly ash, calcium carbonate, carbon black, zinc oxide, graphite, or a combination thereof; more preferably wherein the inorganic filler is treated with a silane coupling agent.

[0086] Aspect 8. The electronic device of any one or more of the preceding aspects, further comprising an additive; preferably wherein the additive is an antioxidant, a heat stabilizer, a light stabilizer, a ultraviolet light stabilizer, a ultraviolet light-absorbing compound, a near infrared light-absorbing compound, an infrared light-absorbing compound, a plasticizer, a lubricant, a release agent, a antistatic agent, an anti-fog agent, an antimicrobial agent, a surface effect additive, a radiation stabilizer, a flame retardant, an anti-drip agent, a fragrance, an adhesion promoter, a flow enhancer, a coating additive, or a combination thereof.

[0087] Aspect 9. The electronic device of any one or more of the preceding aspects, wherein the aromatic dianhydride curing agent comprises bisphenol-A dianhydride and the additional curing promoter comprises methyltetrahydrophthalic anhydride.

[0088] Aspect 10. A method of encapsulating an electronic device of any one or more of the preceding aspects with the curable encapsulation composition, the method comprising: combining the epoxy resin, the curing agent, and the curing catalyst under conditions effective to form a mixture; heating the mixture at a temperature sufficient to soften or liquefy the mixture; and encapsulating at least a portion of the electronic device.

[0089] Aspect 11. The method of aspect 10, wherein the encapsulating comprises flowing the heated mixture into contact with the at least a portion of the electronic device.

[0090] Aspect 12. The method of any one or more of the preceding aspects, further comprising curing the encapsulated portion of the electronic device.

[0091] Aspect 13. The method of aspect 12, wherein the curing comprises heating at a temperature of 120 to 250°C for 2 minutes to 4 hours.

[0092] Aspect 14. An electronic device comprising a cured product of the curable encapsulant composition of any one or more of the preceding aspects.

[0093] Aspect 15. The electronic device of aspect 14, wherein the cured product encapsulates a least a portion of a transistor, a capacitor, a relay, a diode, a resistor, an integrated circuit, or a combination thereof.

[0094] The compositions, methods, and articles can alternatively comprise, consist of, or consist essentially of, any appropriate materials, steps, or components herein disclosed. The compositions, methods, and articles can additionally, or alternatively, be formulated so as to be

devoid, or substantially free, of any materials (or species), steps, or components, that are otherwise not necessary to the achievement of the function or objectives of the compositions, methods, and articles.

[0095] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of “up to 25 wt%, or, more specifically, 5 wt% to 20 wt%”, is inclusive of the endpoints and all intermediate values of the ranges of “5 wt% to 25 wt%,” etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group.

[0096] The singular forms “a” “an,” and “the” include plural referents unless the context clearly dictates otherwise. “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. The terms “first,” “second,” and the like, do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. “Or” means “and/or” unless clearly stated otherwise. Reference throughout the specification to “an aspect” means that a particular element described in connection with the aspect is included in at least one aspect described herein and may or may not be present in other aspects. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various aspects. A “combination thereof” is open and includes any combination comprising at least one of the listed components or properties optionally together with a like or equivalent component or property not listed.

[0097] Unless specified to the contrary herein, all test standards are the most recent standard in effect as of the filing date of this application, or, if priority is claimed, the filing date of the earliest priority application in which the test standard appears. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this application belongs. All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0098] Compounds are described using standard nomenclature. For example, any position not substituted by any indicated group is understood to have its valency filled by a bond as indicated, or a hydrogen atom. A dash (“-”) that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, -CHO is attached through carbon of the carbonyl group.

[0099] The term “hydrocarbyl” refers to a monovalent group containing carbon and

hydrogen. Hydrocarbyl can be alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkylaryl, or arylalkyl as defined below. The term “hydrocarbylene” refers to a divalent group containing carbon and hydrogen. Hydrocarbylene can be alkylene, cycloalkylene, arylenes, alkylarylene, or arylalkylene as defined below. The term “alkyl” means a branched or straight chain, unsaturated aliphatic hydrocarbon group, e.g., methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, and n- and s-hexyl. “Alkenyl” means a straight or branched chain, monovalent hydrocarbon group having at least one carbon-carbon double bond (e.g., ethenyl (-HC=CH_2)). “Alkoxy” means an alkyl group that is linked via an oxygen (i.e., alkyl-O-), for example methoxy, ethoxy, and sec-butyloxy groups. “Alkylene” means a straight or branched chain, saturated, divalent aliphatic hydrocarbon group (e.g., methylene ($\text{-CH}_2\text{-}$) or, propylene ($\text{-(CH}_2\text{)}_3\text{-}$)). “Cycloalkylene” means a divalent cyclic alkylene group, $\text{-C}_n\text{H}_{2n-x}$, wherein x is the number of hydrogens replaced by cyclization(s). “Cycloalkenyl” means a monovalent group having one or more rings and one or more carbon-carbon double bonds in the ring, wherein all ring members are carbon (e.g., cyclopentyl and cyclohexyl). “Aryl” means an aromatic hydrocarbon group containing the specified number of carbon atoms, such as phenyl, tropone, indanyl, or naphthyl. “Arylene” means a divalent aryl group. “Alkylaryl” means an aryl group substituted with an alkyl group. “Arylalkyl” means an alkyl group substituted with an aryl group (e.g., benzyl). “Aryloxy” means an aryl group with the indicated number of carbon atoms attached through an oxygen bridge (-O-). “Amino” means a monovalent radical of the formula —NRR' wherein R and R' are independently hydrogen or a C_{1-30} hydrocarbyl, for example a C_{1-20} alkyl group or a C_{6-30} aryl group. “Halogen” or “halogen atom” means a fluorine, chlorine, bromine, or iodine atom. The prefix “halo” means a group or compound including one more of a fluoro, chloro, bromo, or iodo substituent. A combination of different halo groups (e.g., bromo and fluoro), or only chloro groups can be present. The prefix “hetero” means that the compound or group includes at least one ring member that is a heteroatom (e.g., 1, 2, or 3 heteroatom(s)), wherein the heteroatom(s) is each independently N, O, S, Si, or P.

[0100] Unless substituents are otherwise specifically indicated, each of the foregoing groups can be unsubstituted or substituted, provided that the substitution does not significantly adversely affect synthesis, stability, or use of the compound. “Substituted” means that the compound, group, or atom is substituted with at least one (e.g., 1, 2, 3, or 4) substituents instead of hydrogen, where each substituent is independently nitro (-NO_2), cyano (-CN), hydroxy (-OH), halogen, thiol (-SH), thiocyanate (-SCN), C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} haloalkyl, C_{1-9} alkoxy, C_{1-6} haloalkoxy, C_{3-12} cycloalkyl, C_{5-18} cycloalkenyl, C_{6-12} aryl, C_{7-13} arylalkyl (e.g., benzyl), C_{7-12} alkylaryl (e.g., toluyl), C_{4-12} heterocycloalkyl, C_{3-12} heteroaryl, C_{1-6} alkyl sulfonyl

(-S(=O)₂-alkyl), C₆₋₁₂ arylsulfonyl (-S(=O)₂-aryl), or tosyl (CH₃C₆H₄SO₂-), provided that the substituted atom's normal valence is not exceeded, and that the substitution does not significantly adversely affect the manufacture, stability, or desired property of the compound. When a compound is substituted, the indicated number of carbon atoms is the total number of carbon atoms in the compound or group, including those of any substituents.

[0101] While particular aspects have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

What is claimed is:

1. An electronic device encapsulated by a curable encapsulant composition, the curable encapsulant composition comprising:

- 100 parts by weight of an epoxy resin composition;
- 2 to 200 parts by weight of an aromatic dianhydride curing agent;
- an effective amount of a curing catalyst; and
- an additional curing promoter comprising a monoanhydride;

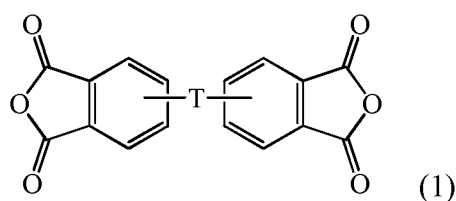
wherein the amounts are based on the total parts by weight of the epoxy resin composition, the aromatic dianhydride curing agent, and the additional curing promoter, and

wherein the curable encapsulant composition after curing has a glass transition temperature of 120 to 320°C, preferably 160 to 320°C, more preferably 180 to 320°C, even more preferably 200 to 320°C, still more preferably 250 to 320°C, as determined by dynamic mechanical analysis.

2. The electronic device of claim 1, wherein the curable encapsulant composition comprises an anhydride to epoxy stoichiometric ratio (A/E) of 0.1:1 to 2.0:1, as determined by molar ratio of total anhydride functionalities to total epoxy functionalities in the curable encapsulant composition.

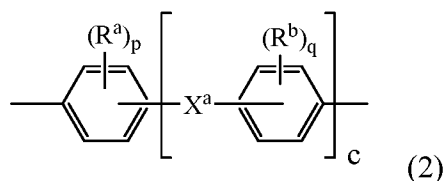
3. The electronic device of any one of the preceding claims, wherein the epoxy resin composition comprises an epoxy resin that is a bisphenol A epoxy resin, a triglycidyl-substituted epoxy resin, a tetraglycidyl-substituted epoxy resin, a bisphenol F epoxy resin, a phenol novolak epoxy resin, a cresol novolak epoxy resin, a cycloaliphatic diglycidyl ester epoxy resin, a cycloaliphatic epoxy resin comprising a ring epoxy group, an epoxy resin containing a spiro-ring, a hydantoin epoxy resin, or a combination thereof;
preferably wherein the epoxy resin composition comprises bisphenol-A diglycidyl ether.

4. The electronic device of any one of the preceding claims, wherein the aromatic dianhydride curing agent has the formula (1)



wherein T is -O-, -S-, -C(O)-, -SO₂-, -SO-, -C_yH_{2y}- wherein y is an integer from 1 to 5 or a halogenated derivative thereof, or -O-Z-O- wherein Z is an aromatic C₆₋₂₄ monocyclic or polycyclic moiety optionally substituted with 1 to 6 C₁₋₈ alkyl groups, 1 to 8 halogen atoms, or a combination thereof;

preferably wherein T is -O- or a group of the formula -O-Z-O- wherein Z is of the formula (2)



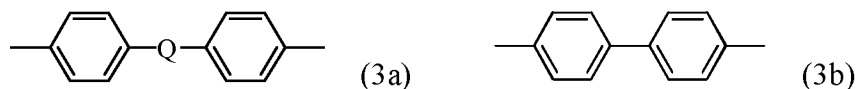
wherein

R^a and R^b are each independently the same or different, and are a halogen atom or a monovalent C₁₋₆ alkyl group,

X^a is a single bond, -O-, -S-, -S(O)-, -S(O)₂-, -C(O)-, or a C₁₋₁₈ organic bridging group, and

p, q, and c are each independently integers of 0 to 4;

more preferably wherein T is a group of the formula -O-Z-O- wherein Z is a divalent group of formulas (3a) or (3b)



wherein Q is -O-, -S-, -C(O)-, -SO₂-, -SO-, -P(R^c)(=O)- wherein R^c is a C₁₋₈ alkyl or C₆₋₁₂ aryl, or -C_yH_{2y}- wherein y is an integer from 1 to 5 or a halogenated derivative thereof;

even more preferably wherein the aromatic dianhydride curing agent comprises bisphenol-A dianhydride.

5. The electronic device of any one of the preceding claims, wherein the additional curing promoter further comprises an amine, a dicyandiamide, a polyamide, an amidoamine, a Mannich base, a phenol-formaldehyde resin, a carboxylic acid functional polyester, a polysulfide, a polymercaptan, an isocyanate, a cyanate ester, or a combination thereof;

preferably wherein the monoanhydride is benzophenone tetracarboxylic anhydride, (C₁₋₆ alkyl)styrene-maleic anhydride copolymer, chlorendic anhydride, dodecenyl succinic anhydride, hexahydrophthalic anhydride, hexahydro-4-methylphthalic anhydride, maleic anhydride, methylbutenyl tetrahydrophthalic anhydride, methylcyclohexene dicarboxylic anhydride, methyl nadic anhydride, methyltetrahydrophthalic anhydride, nadic anhydride, phthalic

anhydride, pyromellitic anhydride, succinic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, or a combination thereof.

6. The electronic device of any one of the preceding claims, wherein the curing catalyst comprises a substituted or unsubstituted C_{3-6} heterocycle comprising 1 to 4 ring heteroatoms, wherein each heteroatom is independently the same or different, and is nitrogen, oxygen, phosphorus, silicon, or sulfur;

preferably wherein the curing catalyst comprises a C_{3-4} five-membered ring wherein the ring heteroatoms are one or two nitrogen atoms.

7. The electronic device of any of the preceding claims, further comprising an inorganic filler, preferably wherein the inorganic filler is fused silica, fumed silica, colloidal silica, aluminum oxide, boron nitride, titanium dioxide, titanium diboride, talc, fly ash, calcium carbonate, carbon black, zinc oxide, graphite, or a combination thereof;

more preferably wherein the inorganic filler is treated with a silane coupling agent.

8. The electronic device of any one of the preceding claims, further comprising an additive; preferably wherein the additive is an antioxidant, a heat stabilizer, a light stabilizer, a ultraviolet light stabilizer, a ultraviolet light-absorbing compound, a near infrared light-absorbing compound, an infrared light-absorbing compound, a plasticizer, a lubricant, a release agent, a antistatic agent, an anti-fog agent, an antimicrobial agent, a surface effect additive, a radiation stabilizer, a flame retardant, an anti-drip agent, a fragrance, an adhesion promoter, a flow enhancer, a coating additive, or a combination thereof.

9. The electronic device of any one of the preceding claims, wherein the aromatic dianhydride curing agent comprises bisphenol-A dianhydride and the additional curing promoter comprises methyltetrahydrophthalic anhydride.

10. A method of encapsulating the electronic device of any one of the preceding claims with the curable encapsulation composition, the method comprising:

combining the epoxy resin, the curing agent, and the curing catalyst under conditions effective to form a mixture;

heating the mixture at a temperature sufficient to soften or liquefy the mixture; and encapsulating at least a portion of the electronic device.

11. The method of claim 10, wherein the encapsulating comprises flowing the heated mixture into contact with the at least a portion of the electronic device.

12. The method of any one of claims 10 and 11, further comprising curing the encapsulated portion of the electronic device.

13. The method of claim 12, wherein the curing comprises heating at a temperature of 120 to 250°C for 2 minutes to 4 hours.

14. An electronic device of any one of the preceding claims, comprising a cured product of the curable encapsulant composition.

15. The electronic device of claim 14, wherein the cured product encapsulates a least a portion of a transistor, a capacitor, a relay, a diode, a resistor, an integrated circuit, or a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2020/020967

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/42 C08G59/68
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2007/231581 A1 (LIN PUI-YAN [US] ET AL) 4 October 2007 (2007-10-04) example 1; table 1 -----	1-8, 10-15 9
X	US 3 336 260 A (SPATZ SYDNEY M ET AL) 15 August 1967 (1967-08-15) example 5 -----	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 April 2020

Date of mailing of the international search report

08/05/2020

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Hoffmann, Michael

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/020967

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CH 427268 A 31-12-1966	
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