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(54) Title: THERMALLY CONDUCTIVE INTERFACE FORMULATIONS AND METHODS THEREOF

(57) Abstract: Provided herein are thermally-conductive interface material formulations having advantageous properties for use within the electronics industry and other industrial applications (e.g. in die attach semiconductor packages, wafer applied underfill film, non-conductive paste, and thermal interface materials). In accordance with an aspect of the invention, the interface formulation contains a thermosetting resin and a surface modified filler. The surface modified filler is a reaction product of a covalently linked moiety of a filler, and a long chain molecule. In additional aspects of the invention, B-staged aliquots and/or a cured or curable films are provided from the compositions according to the present invention. In certain aspects, the invention relates to articles comprising such interface formulations adhered to a suitable substrate therefor.



THERMALLY CONDUCTIVE INTERFACE FORMULATIONS AND METHODS THEREOF

FIELD OF THE INVENTION

[0001] The present invention relates to a thermally conductive interface formulations containing a surface modified filler.

BACKGROUND OF THE INVENTION

[0002] As microelectronic circuitry continues to shrink in size and circuit functionality increases, the heat generated becomes more of a problem for manufacturers and end users. Thermoset formulations, in the form of an interface material, are used as adhesives and fillers in the electronics industry to minimize stress caused by differing coefficients of thermal expansion rates between the electronic components and to transport heat away from heat sources. Applications for interface formulations may include uses as an underfill and as a thermal interface material.

[0003] Typically, an underfill surrounds the periphery of the electronic component and occupies the space between the electronic component and the substrate that is not occupied by solder. Thermal interface materials, also known as "TIMs," improve surface thermal contact at an interface between two component across which heat flow, such as between a heat sink and a printed circuit board, or between a heat sink and a chip carrier.

[0004] Underfill materials and TIMs have been formulated by incorporating thermally conductive filler particles such as alumina into compositions. However, although high loading levels of such filler may provide desirable thermal conductivity, such levels also result in an undesirable higher melt viscosity, reduced flowability, poor processability, and higher storage modulus. High filler content also causes surface dryness and hinders lamination and bonding performance of the underfill and TIMs.

[0005] Consequently, further improvement of a thermally conductive interface formulations are desirable.

BRIEF SUMMARY OF THE INVENTION

[0006] In accordance with the present invention, there are provided a thermally-conductive interface material formulation having advantageous properties for use within the electronics industry and other industrial applications (e.g. in die attach semiconductor packages, wafer applied underfill film, non-conductive paste, and thermal interface materials). In accordance

with an aspect of the invention, the interface formulation contains a thermosetting resin, and a surface modified filler. The surface modified filler is a reaction product of a covalently linked moiety of a filler, and a long chain molecule such as the following:

$Y-(CH_2CH_2O)_m-(CH_2)_q-X$, wherein m is 1 or greater and q is 1 or greater,

$Y-(CH_2)_n-X$, wherein n is 2 or greater, and

$Y-(CF_2)_p(CH_2)_z-X$, wherein p is 1 or greater and z is 1 or greater.

[0007] X represents a functional group that covalently reacts with the filler, and Y represents an end group.

[0008] In accordance with another aspect of the invention, the interface formulation can be a B-staged aliquot and/or a cured or curable film. In certain aspects, the invention relates to articles comprising such interface formulation adhered to a suitable substrate therefor.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Described herein are compositions and methods of making thermally-conductive interface formulations containing a surface modified filler. As defined herein, a surface modified filler is a reaction product of a covalently linked moiety of a filler and a long chain molecule. The surface modified filler enables high filler loading levels, such as at levels greater than 75 wt.%, which results in improved thermal performance, while unexpectedly maintaining performance parameters of melt viscosity, flowability, processability, storage modulus, wettability and bonding performance typically found at conventional loading levels of about 75%. Similarly, disclosed herein are interface formulations having surface modified fillers that at conventional filler loading levels of about 75 wt.%, provides unexpectedly improved melt viscosity, flowability, processability, storage modulus, wettability and bonding performance.

[0010] Without being bound by theory, it is believed that the when a surface modified filler entangles within a thermoset, it acts as a bridge to decrease resistance to thermal flow between the filler and thermoset. Thus, when an energy carrier such as a photon attempts to traverse an interface between a filler and thermoset, it is believed that the covalently bonded long chain molecules reduces the scattering of the energy carrier and improves thermal transfer. At the same time, the long chain molecules improves the compatibility between the filler and the thermoset by improving the wetting or spreading of the filler into the thermoset. This in turn reduces voids, improves processability, and improves mechanical strength of the interface material.

Surface modified filler

[0011] In accordance with the present invention the surface modified filler is a reaction product of a covalently linked moiety of a filler and a long chain molecule.

[0012] Fillers contemplated for use in the practice of the present invention include both non-electrically conductive inorganic fillers and electrically conductive fillers.

[0013] Non-electrically conductive inorganic fillers as defined herein have a thermal conductivity similar to or greater than silica. Such fillers may be selected from broad categories of inorganic materials that include without limitation metals, inorganic oxides, inorganic sulfides, inorganic antimonides, inorganic salts, inorganic nitrides, metallic particles, metal coated particles, for example. Exemplary fillers include aluminum oxide (Al_2O_3), zinc oxide (ZnO), magnesium oxide (MgO), aluminum nitride (AlN), boron nitride (BN), silicon dioxide (SiO_2), diamond, clay, aluminosilicate, and the like, as well as mixtures of any two or more thereof.

[0014] Electrically conductive fillers as defined herein have a thermal conductivity similar to or greater than silica. Such fillers may be selected from broad categories of nanoparticles that include without limitation carbon nanotubes, graphene, fullerene, graphite, silver, gold and any metals and the like, as well as mixtures of any two or more thereof.

[0015] In certain embodiments, inventive formulations includes alumina hydrate particulate material conforming to the formula: $\text{Al}(\text{OH})_a\text{O}_b$, where $0 < a \leq 3$ and $b = (3-a)/2$. In a particular embodiment, the alumina hydrate particulate material is free of non-alumina ceramic materials, and, in particular, is free of silica and aluminosilicate materials. By way of example, when $a=0$ the formula corresponds to alumina (Al_2O_3). Alumina hydrate particulate materials can include aluminum hydroxides, such as ATH (aluminum tri-hydroxide), in mineral forms known commonly as gibbsite, bayerite, or bauxite, or can include alumina monohydrate, also referred to as boehmite.

[0016] The selection of filler size and shape influences the thermal conductivity and mechanical properties of the interface material, including thermal conductivity, impact strength, tensile strength, filler loading, processability, and flowability. For example, smaller particle sizes typically leads to lower interparticle distance and greater chances for the formation of thermal

pathways. At the same time smaller particle sizes may bring more interfacial area for thermal resistance. Greater interparticle distances may allow for greater flowability.

[0017] In an embodiment, the filler employed in invention formulations has a particle size in the range of about 0.005 μm (i.e., 5 nm) up to about 20 μm . In some embodiments, filler employed herein has a particle size in the range of about 0.1 μm up to about 5 μm . In certain embodiments, filler employed herein has a particle size in the range of about 0.2 μm up to about 0.5 μm .

[0018] Long chain molecules for use in the practice of the present invention contain at least one functional group configured to facilitate covalent bonding with the filler. For example, the functional group may undergo a reaction to form a covalent bond with oxygen of a hydroxyl group on the surface of the filler. The functional group may facilitate nucleophilic substitution or nucleophilic addition with a hydroxyl group on the surface of the filler, such as forming a covalent bond with oxygen of the hydroxyl group in place of the hydrogen.

[0019] In certain embodiments, the long chain molecule is selected from the group consisting of

$\text{Y}-(\text{CH}_2\text{CH}_2\text{O})_m-(\text{CH}_2)_q-\text{X}$, wherein m is at least 1 or greater and q is at least 1 or greater,

$\text{Y}-(\text{CH}_2)_n-\text{X}$, wherein n is 2 or greater,

$\text{Y}-(\text{CF}_2)_n-\text{X}$, wherein n is 2 or greater, and

$\text{Y}-(\text{CF}_2)_p(\text{CH}_2)_z-\text{X}$.

[0020] X represents a functional group that covalently reacts with the filler. X can be selected from the following: trialkoxysilane, such as trimethoxysilane and triethoxysilane, isocyanate, carboxylic acid, anhydride, maleate, fumarate, sulfonic acid, acyl chloride, or epoxide.

Additional X functional groups include halogen atoms, such as fluorine, chlorine, or bromine, and sulfatoethylsulfone, silanol, zirconate, titanate, esters, aldehyde, phosphonic acid, trialkoxysilane, such as trimethoxysilane and triethoxysilane, isocyanate, carboxylic acid, anhydride, maleate, fumarate, sulfonic acid, acyl chloride, epoxide, and the like.

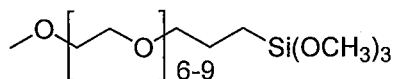
[0021] The long chain molecule may also include an additional Y group that is a nonreactive end group or a functional group that is capable of polymerization with or without crosslinking. The Y groups may include an acrylate, methacrylate, anhydride, NH_2 , aromatic amine, epoxy, styrene, maleate, fumarate, vinyl ether, oxetane, benzoxazine, cyanate ester, maleimide, vinyl

ester, phenol, mercaptan, isocyanate, an alkyl, an alkoxide, trifluoro cinnamyl, propargyl ether, oxazoline, and the like.

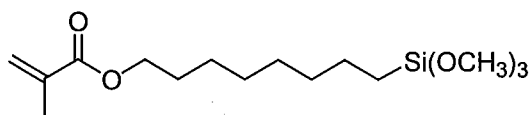
[0022] Long chain molecules of $Y-(CH_2CH_2O)_m-(CH_2)_q-X$, wherein m is at least 1 or greater and q is at least 1 or greater include polyethylene oxide (PEO) units between 6 and 9. In an embodiment, m is between 6 and 9, and q is 1 or greater. The optimum quantity of polyethylene oxide units depends to some extent on the sequence length of CH_2 units. It is believed that a length of m between 6 to 9 is the ideal length for forming a single layer of organic molecules on the filler surface. It is believed that lengths longer than this may result in a formation of a thick layer on the filler resulting in an increase in thermal resistance. It was further surprisingly discovered that long chain PEO molecules provide significantly improved wetting ability and compatability with resins as compared to aliphatic long chain acrylates.

[0023] Without being bound by theory, it is believed that functional groups such as silane molecules act as bridge between filler and resin and decrease interface resistance, where photons are easily scattered. At the same time the functional groups can improve the wetting and compatibility between filler and resin matrix.

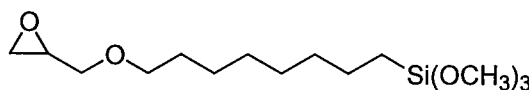
[0024] Exemplary long chain molecules of $Y-(CH_2CH_2O)_m-(CH_2)_q-X$ include methoxytriethyleneoxypropyltrimethoxysilane, 2-[methoxy(polyethyleneoxy)9-12-propyl]-trimethoxysilane, 2-[(acetoxypolyethyleneoxy)propyl]triethoxysilane, [hydroxy(polyethyleneoxy)propyl]triethoxysilane, triethoxysilylpropoxy(polyethyleneoxy)dodecanoate, 2-[methoxy(polyethyleneoxy)6-9-propyl]-trimethoxysilane, and the like. For example, 2-[methoxy(polyethyleneoxy)6-9-Propyl]-trimethoxysilane is shown below:



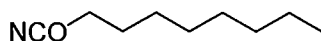
[0025] Long chain molecules of $Y-(CH_2)_n-X$, wherein n is 2 or greater, contemplated herein include silane molecules having a trialkoxysilane and a methacrylate functionality. Exemplary molecules include methacryloxyheptyl trimethoxysilane, methacryloxyhexyl trimethoxysilane, methacryloxyoctyl trimethoxysilane, and the like. For example, methacryloxyoctyl trimethoxysilane is shown below:



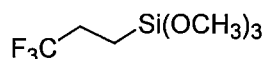
[0026] Additional examples of $Y-(CH_2)_n-X$, wherein n is 2 or greater, contemplated herein include ethers with a trialkoxysilane and epoxy functionality such as (3-glycidyloxyoctyl)trimethoxysilane shown below:



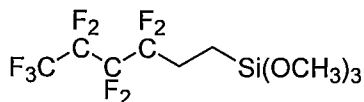
[0027] Additional examples of $Y-(CH_2)_n-X$, wherein n is 2 or greater includes molecules having an isocyanate reactive functionality. In an embodiment, the molecule is an octyl isocyanate such as shown below:



[0028] Further examples of $Y-(CH_2)_n-X$, wherein n is 2 or greater includes molecules having X as a silane group and Y as a trifluoromethyl group and identified trimethoxy(3,3,3-trifluoropropyl)silane, which is shown below:



[0029] Long chain molecules also include fluorinated molecules including $Y-(CF_2)_p(CH_2)_z-X$, wherein p is 1 or greater and z is 1 or greater. In an embodiment, $Y-(CF_2)_p(CH_2)_z-X$ wherein p is 2 or greater, z is 2 or greater, X is a silane group includes molecules having a trifluoromethyl groups. Exemplary molecules include (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane, (nonafluoro-1,1,2,2-tetrahydrohexyl)triethoxysilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane, nonafluoro-1,1,2,2-tetrahydrohexyl)trimethoxysilane, and the like. For example, nonafluoro-1,1,2,2-tetrahydrohexyl)trimethoxysilane is shown below:



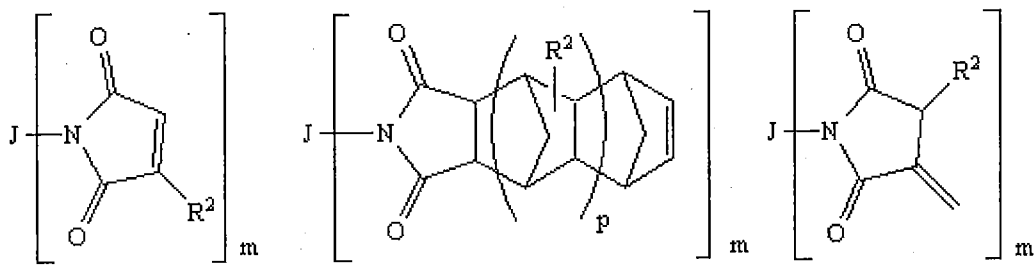
[0030] Without being bound by theory, it is believed that fluorine substitution renders the chemical bonds of the long chain molecule more electronegative, which in turn makes modified fillers more compatible with resin matrix, e.g. trimethoxy(3,3,3-trifluoropropyl)silane. However, too much fluorine substitution may result in formation of an hydrophobic insulative layer that is less compatible with resin matrix, e.g. nonafluoro-1,1,2,2-tetrahydrohexyl)trimethoxysilane.

[0031] In an embodiment, surface modified filler in an interface formulation comprises in the range of about 60 wt. % up to about 95 wt. % of said surface modified filler. In some embodiments, surface modified filler comprises in the range of about 70 wt. % up to about 85 wt. % of said surface modified filler. In certain embodiments, surface modified filler comprises in the range of about 75 wt. % up to about 80 wt. % of said surface modified filler.

Thermosetting resin

[0032] Exemplary thermosetting resin compositions contemplated for use herein include maleimides, nadimides, itaconamides, epoxies, (meth)acrylates, cyanate esters, vinyl group-containing resins, cyclic esters (e.g., ϵ -caprolactone), benzoxazines, oxetanes, silicone resins, polyester, polyurethane, polyimide, melamine, urea-formaldehyde, phenol-formaldehyde, and the like, as well as mixtures of any two or more thereof.

[0033] Exemplary maleimides, nadimides, or itaconimides contemplated for use herein include compounds having the structure:



respectively, wherein:

m is 1-15,

p is 0-15,

each R^2 is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent radical selected from:

- hydrocarbyl or substituted hydrocarbyl species typically having in the range of about 6 up to about 500 carbon atoms, where the hydrocarbyl species is selected from alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, alkylaryl, arylalkyl, aryalkenyl, alkenylaryl, arylalkynyl or alkynylaryl;
- hydrocarbylene or substituted hydrocarbylene species typically having in the range of about 6 up to about 500 carbon atoms, where the hydrocarbylene species are selected from alkylene, alkenylene, alkynylene, cycloalkylene, cycloalkenylene, arylene, alkylarylene, arylalkylene, arylalkenylene, alkenylarylene, arylalkynylene or alkynylarylene,
- aromatic hydrocarbyl or substituted aromatic hydrocarbyl species having in the range of about 6 up to about 300 carbon atoms, where the aromatic hydrocarbyl species is selected from aryl, alkylaryl, arylalkyl, aryalkenyl, alkenylaryl, arylalkynyl or alkynylaryl;
- aromatic hydrocarbylene or substituted aromatic hydrocarbylene species having in the range of about 6 up to about 300 carbon atoms, where the aromatic hydrocarbylene species are selected from arylene, alkylarylene, arylalkylene, arylalkenylene, alkenylarylene, arylalkynylene or alkynylarylene,
- heterocyclic or substituted heterocyclic species having in the range of about 6 up to about 300 carbon atoms,
- polysiloxane, or
- polysiloxane-polyurethane block copolymers, as well as

combinations of one or more of the above with a linker selected from a covalent bond, -O-, -S-, -NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -O-S(O)₂-, -O-S(O)₂-O-, -O-S(O)₂-NR-, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, -S-S(O)₂-, -S-S(O)₂-O-, -S-S(O)₂-NR-, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, -NR-O-S(O)₂-, -NR-O-S(O)₂-O-, -NR-O-S(O)₂-NR-, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, -O-NR-S(O)₂-O-, -O-NR-S(O)₂-NR-, -O-NR-S(O)₂-,

-O-P(O)R₂-, -S-P(O)R₂-, or -NR-P(O)R₂-; where each R is independently hydrogen, alkyl or substituted alkyl.

[0034] Compositions according to the present invention include compounds wherein J is oxyalkyl, thioalkyl, aminoalkyl, carboxylalkyl, oxyalkenyl, thioalkenyl, aminoalkenyl, carboxyalkenyl, oxyalkynyl, thioalkynyl, aminoalkynyl, carboxyalkynyl, oxycycloalkyl, thiocycloalkyl, aminocycloalkyl, carboxycycloalkyl, oxycycloalkenyl, thiocycloalkenyl, aminocycloalkenyl, carboxycycloalkenyl, heterocyclic, oxyheterocyclic, thioheterocyclic, aminoheterocyclic, carboxyheterocyclic, oxyaryl, thioaryl, aminoaryl, carboxyaryl, heteroaryl, oxyheteroaryl, thioheteroaryl, aminoheteroaryl, carboxyheteroaryl, oxyalkylaryl, thioalkylaryl, aminoalkylaryl, carboxyalkylaryl, oxyarylalkyl, thioarylalkyl, aminoarylalkyl, carboxyarylalkyl, oxyarylalkenyl, thioarylalkenyl, aminoarylalkenyl, carboxyarylalkenyl, oxyalkenylaryl, thioalkenylaryl, aminoalkenylaryl, carboxyalkenylaryl, oxyarylalkynyl, thioarylalkynyl, aminoarylalkynyl, carboxyarylalkynyl, oxyalkynylaryl, thioalkynylaryl, aminoalkynylaryl or carboxyalkynylaryl, oxyarylene, thioarylene, aminoarylene, carboxyarylene, oxyalkylarylene, thioalkylarylene, aminoalkylarylene, carboxyalkylarylene, oxyarylalkylene, thioarylalkylene, aminoarylalkylene, carboxyarylalkylene, oxyarylalkenylene, thioarylalkenylene, aminoarylalkenylene, carboxyarylalkenylene, oxyalkenylarylene, thioalkenylarylene, aminoalkenylarylene, carboxyalkenylarylene, oxyarylalkynylene, thioarylalkynylene, aminoarylalkynylene, carboxyarylalkynylene, oxyalkynylarylene, thioalkynylarylene, aminoalkynylarylene, carboxyalkynylarylene, heteroarylene, oxyheteroarylene, thioheteroarylene, aminoheteroarylene, carboxyheteroarylene, heteroatom-containing di- or polyvalent cyclic moiety, oxyheteroatom-containing di- or polyvalent cyclic moiety, thioheteroatom-containing di- or polyvalent cyclic moiety, aminoheteroatom-containing di- or polyvalent cyclic moiety, or a carboxyheteroatom-containing di- or polyvalent cyclic moiety.

[0035] Exemplary epoxy monomers contemplated for use in the practice of the present invention are described below. Examples of an alicyclic epoxy resin include Denacol (registered trademark) EX-252 (manufactured by Nagase ChemteX Corporation), EPICLON (registered trademark) 200 and 400 (manufactured by DIC Corporation), and jER (registered trademark) 871 and 872 (manufactured by Mitsubishi Chemical Corporation). Examples of a bisphenol A epoxy resin include jER (registered trademark) 828, 834, 1001, and 1004 (manufactured by Mitsubishi Chemical Corporation), and EPICLON (registered trademark) 850, 860, and 4055 (manufactured

by DIC Corporation). Examples of a bisphenol F epoxy resin include jER (registered trademark) 807 (manufactured by Mitsubishi Chemical Corporation) and EPICLON (registered trademark) 830 (manufactured by DIC Corporation). Examples of a phenol novolac epoxy resin include EPICLON (registered trademark) N-740, N-770, and N-775 (manufactured by DIC Corporation) and jER (registered trademark) 152 and 154 (manufactured by Mitsubishi Chemical Corporation). Examples of a cresol novolac epoxy resin include EPICLON (registered trademark) N-660, N-665, N-670, N-673, N-680, N-695, N-665-EXP, and N-672-EXP (manufactured by DIC Corporation). Examples of a glycidylamine epoxy resin include EPICLON (registered trademark) 430 and 430-L (manufactured by DIC Corporation), TETRAD (registered trademark)-C, TETRAD (registered trademark)-X (manufactured by Mitsubishi Gas Chemical Company), jER (registered trademark) 604 and 630 (manufactured by Mitsubishi Chemical Corporation), SUMI-EPDXY (registered trademark) ELM120, ELM100, ELM434, and ELM434HV (manufactured by Sumitomo Chemical Co., Ltd.), and EPOTOHTO (registered trademark) YH-434 and YH-434 L (manufactured by Tohto Kasei Co., Ltd.). Mixtures of any two or more thereof may also be present.

[0036] Additional exemplary epoxy monomers contemplated for use herein include diepoxides of the cycloaliphatic alcohol, hydrogenated bisphenol A (commercially available as Epalloy 5000), difunctional cycloaliphatic glycidyl esters of hexahydrophthalic anhydride (commercially available as Epalloy 5200), Epiclon EXA-835LV, Epiclon HP-7200L, and the like, as well as mixtures of any two or more thereof.

[0037] When epoxy monomer(s) are present in invention compositions, the resulting formulation comprises in the range of about 0.5 - 20 wt % of said epoxy. In certain embodiments, the resulting formulation comprises in the range of about 1-10 wt % of said epoxy.

[0038] When epoxy monomer(s) are present in invention formulations, an epoxy cure agent is also present. Exemplary epoxy cure agents include ureas, aliphatic and aromatic amines, amine hardeners, polyamides, imidazoles, dicyandiamides, hydrazides, urea-amine hybrid curing systems, free radical initiators (e.g., peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, azo compounds, and the like), organic bases, transition metal catalysts, phenols, acid anhydrides, Lewis acids, and Lewis bases.

[0039] When present, invention compositions comprise in the range of about 0.01 - 5 wt % of said epoxy cure agent. In certain embodiments, invention compositions comprise in the range of about 0.05 - 1 wt % of epoxy cure agent.

[0040] Oxetanes (obtained from 1,3-propylene oxide), are heterocyclic organic compounds containing an oxetane ring, i.e., a ring having the molecular formula C_3H_6O (i.e., a four-membered ring with three carbon atoms and one oxygen atom).

[0041] Exemplary acrylates contemplated for use herein include monofunctional (meth)acrylates, difunctional (meth)acrylates, trifunctional (meth)acrylates, polyfunctional (meth)acrylates, and the like.

[0042] Exemplary monofunctional (meth)acrylates include phenylphenol acrylate, methoxypolyethylene acrylate, acryloyloxyethyl succinate, fatty acid acrylate, methacryloyloxyethylphthalic acid, phenoxyethylene glycol methacrylate, fatty acid methacrylate, β -carboxyethyl acrylate, isobornyl acrylate, isobutyl acrylate, t-butyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, dihydrocyclopentadiethyl acrylate, cyclohexyl methacrylate, t-butyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, 4-hydroxybutyl acrylate, tetrahydrofurfuryl acrylate, benzyl acrylate, ethylcarbitol acrylate, phenoxyethyl acrylate, methoxytriethylene glycol acrylate, monopentaerythritol acrylate, dipentaerythritol acrylate, tripentaerythritol acrylate, polypentaerythritol acrylate and the like.

[0043] Exemplary difunctional (meth)acrylates include hexanediol dimethacrylate, hydroxyacryloyloxypropyl methacrylate, hexanediol diacrylate, urethane acrylate, epoxyacrylate, bisphenol A-type epoxyacrylate, modified epoxyacrylate, fatty acid-modified epoxyacrylate, amine-modified bisphenol A-type epoxyacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A dimethacrylate, tricyclodecanedimethanol dimethacrylate, glycerin dimethacrylate, polypropylene glycol diacrylate, propoxylated ethoxylated bisphenol A diacrylate, 9,9-bis(4-(2-acryloyloxyethoxy)phenyl) fluorene, tricyclodecane diacrylate, dipropylene glycol diacrylate, polypropylene glycol diacrylate, PO-modified neopentyl glycol diacrylate, tricyclodecanedimethanol diacrylate, 1,12-dodecanediol dimethacrylate, and the like.

[0044] Exemplary trifunctional (meth)acrylates include trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, trimethylolpropane ethoxy triacrylate, polyether triacrylate, glycerin propoxy triacrylate, and the like.

[0045] Exemplary polyfunctional (meth)acrylates include dipentaerythritol polyacrylate, dipentaerythritol hexaacrylate, pentaerythritol tetraacrylate, pentaerythritolethoxy tetraacrylate, ditrimethylolpropane tetraacrylate, and the like.

[0046] Additional exemplary acrylates contemplated for use in the practice of the present invention include those described in US Pat. No. 5,717,034, the entire contents of which are hereby incorporated by reference herein.

[0047] Cyanate ester monomers contemplated for use in the practice of the present invention contain two or more ring forming cyanate ($-O-C\equiv N$) groups which cyclotrimerize to form substituted triazine rings upon heating. Because no leaving groups or volatile byproducts are formed during curing of the cyanate ester monomer, the curing reaction is referred to as addition polymerization. Suitable polycyanate ester monomers that may be used in the practice of the present invention include, for example, 1,1-bis(4-cyanatophenyl)methane, 1,1-bis(4-cyanatophenyl)ethane, 2,2-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)-2,2-butane, 1,3-bis[2-(4-cyanatophenyl)propyl]benzene, bis(4-cyanatophenyl)ether, 4,4'-dicyanatodiphenyl, bis(4-cyanato-3,5-dimethylphenyl)methane, tris(4-cyanatophenyl)ethane, cyanated novolak, 1,3-bis[4-cyanatophenyl-1-(1-methylethylidene)]benzene, cyanated phenoldicyclopentadiene adduct, and the like. Polycyanate ester monomers utilized in accordance with the present invention may be readily prepared by reacting appropriate dihydric or polyhydric phenols with a cyanogen halide in the presence of an acid acceptor.

[0048] Monomers that can optionally be combined with polycyanate ester monomer(s) in accordance with the present invention are selected from those monomers which undergo addition polymerization. Such monomers include vinyl ethers, divinyl ethers, diallyl ethers, dimethacrylates, dipropargyl ethers, mixed propargyl allyl ethers, monomaleimides, bismaleimides, and the like. Examples of such monomers include cyclohexanedimethanol monovinyl ether, trisallylcyanurate, 1,1-bis(4-allyloxyphenyl)ethane, 1,1-bis(4-propargyloxyphenyl)ethane, 1,1-bis(4-allyloxyphenyl-4'-propargyloxyphenyl)ethane, 3-(2,2-dimethyltrimethylene acetal)-1-maleimidobenzene, 2,2,4-trimethylhexamethylene-1,6-bismaleimide, 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane, and the like.

[0049] Vinyl group-containing resins contemplated for use in the practice of the present invention refer to any resin having one or more vinyl groups ($-\text{CH}=\text{CH}_2$) thereon.

[0050] Polyesters contemplated for use in the practice of the present invention refer to condensation polymers formed by the reaction of polyols (also known as polyhydric alcohols), with saturated or unsaturated dibasic acids. Typical polyols used are glycols such as ethylene glycol; acids commonly used are phthalic acid and maleic acid. Water, a by-product of esterification reactions, is continuously removed, driving the reaction to completion. The use of unsaturated polyesters and additives such as styrene lowers the viscosity of the resin. The initially liquid resin is converted to a solid by cross-linking chains. This is done by creating free radicals at unsaturated bonds, which propagate to other unsaturated bonds in adjacent molecules in a chain reaction, linking the adjacent chains in the process.

[0051] Polyurethanes contemplated for use in the practice of the present invention refer to polymers composed of a chain of organic units joined by carbamate (urethane) links. Polyurethane polymers are formed by reacting an isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule.

[0052] Polyimides contemplated for use in the practice of the present invention refer to polymers composed of a chain of organic units joined by imide linkages (i.e., $-\text{C}(\text{O})-\text{N}(\text{R})-\text{C}(\text{O})-$). Polyimide polymers can be formed by a variety of reactions, i.e., by reacting a dianhydride and a diamine, by the reaction between a dianhydride and a diisocyanate, and the like.

[0053] Melamines contemplated for use in the practice of the present invention refer to hard, thermosetting plastic materials made from melamine (i.e., 1,3,5-triazine-2,4,6-triamine) and formaldehyde by polymerization. In its butylated form, it can be dissolved in n-butanol and/or xylene. It can be used to cross-link with other resins such as alkyd, epoxy, acrylic, and polyester resins.

[0054] Urea-formaldehydes contemplated for use in the practice of the present invention refers to a non-transparent thermosetting resin or plastic made from urea and formaldehyde heated in the presence of a mild base such as ammonia or pyridine.

[0055] Phenol-formaldehydes contemplated for use in the practice of the present invention refer to synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde.

[0056] In one aspect, interface compositions comprise in the range of about 10 - 50 wt % of said thermosetting resin compositions. In certain embodiments, invention compositions comprise in the range of about 15-25 wt % of said thermosetting resin compositions. Invention compositions typically comprise in the range of about 0.05 - 2 wt % of said free-radical polymerization initiator. In certain embodiments, invention compositions comprise in the range of about 0.1-1 wt % of said free radical polymerization initiator.

[0057] In certain embodiments, invention compositions further comprise a radical stabilizer. When present, radical stabilizers contemplated for use herein include hydroquinones, benzoquinones, hindered phenols, benzotriazole-based ultraviolet absorbers, triazine-based ultraviolet absorbers, benzophenone-based ultraviolet absorbers, benzoate-based ultraviolet absorbers, hindered amine -based ultraviolet absorbers, and the like, as well as combinations of any two or more thereof.

[0058] When present, invention compositions comprise in the range of about 0.1 - 1 wt % of said radical stabilizer. In some embodiments, invention compositions comprise in the range of about 0.1-0.6 wt % of said radical stabilizer.

[0059] In certain embodiments, invention formulations optionally further comprise a non-reactive diluent. Exemplary diluents contemplated for use herein, when present, include aromatic hydrocarbons (e.g., benzene, toluene, xylene, and the like), saturated hydrocarbons (e.g., hexane, cyclohexane, heptane, tetradecane), chlorinated hydrocarbons (e.g., methylene chloride, chloroform, carbon tetrachloride, dichloroethane, trichloroethylene, and the like), ethers (e.g., diethyl ether, tetrahydrofuran, dioxane, glycol ethers, monoalkyl or dialkyl ethers of ethylene glycol, and the like), polyols (e.g., polyethylene glycol, propylene glycol, polypropylene glycol, and the like), esters (e.g., ethyl acetate, butyl acetate, methoxy propyl acetate, and the like); dibasic esters, alpha-terpineol, beta-terpineol, kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, carbitol acetate, ethyl carbitol acetate, hexylene glycol, high boiling alcohols and esters thereof, glycol ethers, ketones (e.g., acetone, methyl ethyl ketone, and the like), amides (e.g., dimethylformamide, dimethylacetamide, and the like), heteroaromatic compounds (e.g., N-methylpyrrolidone, and the like), and the like, as well as mixtures of any two or more thereof.

[0060] When present for film, underfill and TIM applications, the interface compositions comprises in the range of about 10 up to about 70 wt % of a nonreactive diluent, based on the

total weight of the formulation. In certain embodiments, invention compositions comprise in the range of about 10 - 50 wt % diluent, relative to the total composition. In certain embodiments, invention compositions comprise in the range of about 20-40 wt % diluent. For film casting and B-stage processes, the non-reactive diluent is typically dried off from the system and the final film product typically contains a small amount of diluent residue, such as <2% at 250°C by TGA.

Other additives

[0061] Compositions according to the present invention may optionally further comprise one or more flow additives, adhesion promoters, conductivity additives, rheology modifiers, toughening agents, fluxing agents, and the like, as well as mixtures of any two or more thereof. Exemplary compounds which impart such properties include silicon polymers, ethyl acrylate/2-ethylhexyl acrylate copolymers, alkylol ammonium salts of phosphoric acid esters of ketoxime, and the like, as well as combinations of any two or more thereof.

[0062] Exemplary interface compositions according to the present invention comprise:

- at least 10 wt. % thermosetting resin,
- at least 0.05 wt. % curing agent, and
- at least 60 wt. % surface modified filler.

[0063] Additional exemplary compositions according to the present invention comprise:

- 10 - 50 wt. % thermosetting resin,
- 0.05 - 2 wt. % curing agent,
- 60 - 95 wt. % surface modified filler.

[0064] In certain embodiments, still further exemplary compositions according to the present invention comprise:

- 15 - 25 wt. % thermosetting resin,
- 0.01 - 1 wt. % curing agent,
- 70 - 85 wt. % surface modified filler.

[0065] In an embodiment of the formulation, the filler is an inorganic filler selected from the group consisting of aluminum oxide, aluminum nitride, boron nitride, aluminum oxide, aluminum nitride, magnesium oxide, zinc oxide, silicon carbide, silicon dioxide, beryllium oxide, antimony oxide, and mixtures thereof. In a specific embodiment of the formulation, the

filler is aluminum oxide. In another embodiment, the filler is selected from the group consisting of carbon nanotubes, graphene, fullerene, and graphite.

[0066] In accordance with another embodiment, the filler in formulation is at least 75 wt.% aluminum oxide, and upon cure the formulation exhibits a melt viscosity less than 35,000 P and a storage modulus less than 15 GPa.

[0067] In accordance with yet another embodiment, the filler in the formulation is at least 80 wt.% aluminum oxide, and upon cure the formulation exhibits an a bulk thermal conductivity upon cure greater than 1.4 W/mK; in some embodiments, upon cure the filler imparts a melt viscosity less than 30,000 P, and a storage modulus less than 15 GPa.

[0068] In accordance with further embodiment of the invention, the formulation is a B-staged aliquot. In some embodiments, the formulation is a cured aliquot. In other embodiments, a curable film comprises a B-staged layer of the formulation on a suitable substrate.

[0069] In accordance with yet another embodiment of the present invention, there are provided methods for adhesively attaching a first article to a second article, said method comprising:

- (a) applying an aliquot of the aforementioned formulation to said first article,
- (b) bringing said first and second articles into intimate contact to form an assembly wherein the space between said first article and said second article is substantially completely filled by the formulation applied in step (a), and thereafter
- (c) optionally subjecting said assembly to conditions suitable to cure said formulation.

[0070] The process for making the surface modified filler are illustrated in the examples in this specification. Several methods of surface hydroxylization are well known and the choice depends on the selected filler used. Examples include immersion in water, treatment with laser light, hydrogen peroxide, or ozone.

[0071] Long chain molecules are then covalently attached to the hydroxylized surface via various conjugation strategies. The filler can be covalently linked by a condensation reaction (by reaction with hydroxyl groups of a hydrolyzed silane), by ester formation (by reaction with an anhydride, an acid chloride or even an acid), amide formation (by reaction with isocyanates) or ether formation (by reaction with alkyl halides).

[0072] The interface material can be in the form of a viscous liquid, paste, gel, film, suspension, or slurry. The interface material can then be dried and stabilized, partially cured, or otherwise

solidified. Applications for the interface material include wafer applied underfill film (WAUF), non-conductive paste (NCP), and and/or TIMs.

[0073] A B-stage underfill film is manufactured by applying the underfill resin composition of the present invention to a support base film to form a resin composition layer, and if necessary, drying the layer. In one embodiment, the thermoset, surface modified filler, curing agent, additives, and diluents are stirred at room temperature for at least 30 minutes to obtain a varnish. The varnish is then cast on a base film and a film is then prepared by evaporating off the solvent.

[0074] Various aspects of the present invention are illustrated by the following non-limiting example. The example is for illustrative purposes and is not a limitation on any practice of the present invention. It will be understood that variations and modifications can be made without departing from the spirit and scope of the invention. One of ordinary skill in the art readily knows how to synthesize or commercially obtain the reagents and components described herein.

EXAMPLES

[0075] Compositions were prepared containing each of the components contemplated above, i.e.,
at least 10 wt % thermosetting resin,
at least 0.05 wt % curing agent, and
at least 60 wt % surface modified filler.

[0076] Surface modified fillers were prepared by refluxing alumina, solvent and excess of the long chain molecules overnight. The fillers were then washed off by solvent and dried at vacuum. The surface modified fillers were then blended with the thermosetting resins and other components listed above. A varnish was made using solvent to dissolve or disperse all the components. The varnish was coated on PET based release liner, and then B-staged inside an oven to dry off the solvent without curing at this point. B-stage conditions varied depending on the components, such as between 60°C to 150°C for 1 to 10 minutes.

Example 1: 75% Loading of Interface Formulation

[0077] Interface compositions were prepared as shown in Table 1. Each of the compositions prepared for Control 1 and Inventive Samples 1A and 1B contain the same quantity of alumina filler components (75%). Control 1 contains untreated alumina, while Samples 1A and 1B contain surface modified alumina fillers.

Table 1

Component		Sample (wt. %)		
Type	Identity	Control 1	Invention Sample #1A	Invention Sample #1B
Filler	Alumina	75		
Surface Modified Filler	Alumina covalently linked with long chain molecule:			
	Methacryl-oxyoctyl-trimethoxy-silane		75	
	2[Methoxy(polyethyleneoxy)6-9-Propyl]-trimethoxysilane			75
Toughening agent	Polymers	10.2	10.2	10.2
Acrylate resin	SR368	5	5	5
Epoxy resin	Epicon N665-EXP	1.3	1.3	1.3
hardener	2PHZ	0.1	0.1	0.1
bismaleimide resin	BMI resin	6.0	6.0	6.0
Adhesion promoter	Adhesion promoter	0.7	0.7	0.7
Radical initiator	Dicumyl peroxide	0.3	0.3	0.3
Fluxing agent	Glutaric acid	1.3	1.3	1.3
Radical inhibitor	8-Hydroxyquinoline	0.1	0.1	0.1

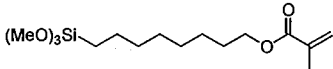
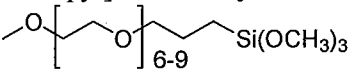
[0078] Various performance properties of the above-described formulations were tested and the results are summarized in Tables 2 below.

[0079] In package thermal resistance was performed by embedding a sample film in a QFN package with thermal die and placing in thermal test machine called a T3Ster.

[0080] Melt viscosity is measured by Area Rheometer at 10 Rad frequency with a 10°C/min ramp rate using 1mm thick 1 inch in diameter samples. Transmittance was measured by Perkin Elmer LAMBDA 35 series UV Spectrometer to check how much light is transmitted through film. Storage modulus was measured by dynamic mechanical analysis (DMA). The glass transition temperature (T_g) was measured by Thermomechanical analysis. Bulk thermal conductivity was measured by laser flash.

[0081] As shown in Table 2, at 75% filler loading, Inventive Samples 1A and 1B achieved a significantly lower in-package thermal resistance compared to Control 1. Further, the inventive samples resulted in a composition having a lower melt viscosity, weight loss, and storage modulus, while improving flowability, providing a faster cure, while maintaining thermal conductivity and transparency.

Table 2

	Unit	Control 1	Invention Sample #1A	Invention Sample #2A
Filler type	-	Alumina	Alumina	Alumina
Long Chain Molecule		None	Methacryl-oxyoctyl- trimethoxy-silane 	2-[Methoxy(polyethyleneoxy)6-9-Propyl]-trimethoxysilane 
Filler loading	Wt.%	75	75	75
	Vol.%	49.6	49.6	49.6
In-pkg thermal resistance Rth	K/W	2.8	2.2	2.1
Bulk thermal conductivity	W/mK	1.08-1.3	0.8-1.1	0.9-1.3
Transmittance @555nm	%	67.4	66.8	62.6
Melt Viscosity	P	44,604 - 74,230	25,360	20,210
Lowest MV temperature	°C	94 -112	111	112
DSC onset temp	°C	141	136	140
DSC peak temp	°C	169	156	153
B-stage TGA at 250°C	%	1.41	1.13	0.44
DMA Storage Modulus @25°C	GPa	15.6-20.4	13.6	9.8

Example 2: 80% Loading of Interface Formulation

[0082] Interface compositions were prepared as shown in Table 3. Control 2 and Inventive Samples 2A, 2B and 2C contain the same quantity of alumina filler components (80%). Control

2 contains untreated alumina, while Samples 2A, 2B, and 2C contain surface modified alumina fillers.

Table 3

Component		Sample (wt. %)			
Type	Identity	Control 2	Invention Sample #2A	#2B	#2C
Filler	Alumina	80			
Surface Modified Filler	Alumina covalently linked with long chain molecule:				
	Octyl isocyanate		80		
	Methacryl-oxyoctyl-trimethoxy-silane			80	
	2[Methoxy(polyethyleneoxy)6-9-propyl]-trimethoxysilane				80
Toughening agent	Polymers	7.6	7.6	7.6	7.6
Acrylate resin	SR368	5.0	5.0	5.0	5.0
Epoxy resin	Epicon N665-EXP	5.0	5.0	5.0	5.0
hardener	2PHZ	0.1	0.1	0.1	0.1
bismaleimide resin	BMI resin	5.0	5.0	5.0	5.0
Adhesion promoter	Adhesion promoter	1.0	1.0	1.0	1.0
Radical initiator	Dicumyl peroxide	0.25	0.25	0.25	0.25
Fluxing agent	Glutaric acid	1.0	1.0	1.0	1.0
Radical inhibitor	8-Hydroxyquinoline	0.2	0.2	0.2	0.2

[0083] Various performance properties of the above-described formulations were tested and the results are summarized in Tables 4 below. At 80% filler loading, the inventive interface formulations 2A, 2B and 2C achieved high thermal conductivity, while maintaining low modulus, melt viscosity, film processibility as compared to Control 1. Regarding Control 2, at 80% filler level, a film could not be formed in all likelihood due to its dryness, and the properties could not be evaluated.

Table 4

	Unit	Control 1	Control 2	Invention Sample #2A	Invention Sample #2B	Invention Sample #2C
Filler type	-	Alumina	Alumina	Alumina	Alumina	Alumina
Long chain molecule	-	None	None	Octyl isocyanate	Methacryloxyoctyl-trimethoxysilane	2-[Methoxy(polyethyleneoxy)6-9-Propyl]-trimethoxysilane
Filler loading	Wt%	75	80	80	80	80
Melt Viscosity	P	42,400	N/A	49,000	44,400	37,800
Lowest MV temperature	°C	100	N/A	107	103	104
Bulk thermal conductivity	W/m K	1.34	N/A	2.08	1.52	1.45
Storage Modulus @25	GPa	20.4	N/A	13.6	14.9	14.0
B-stage TGA at 250°C	%	1.41	N/A	0.83	1.87	0.83
Transmittance @555nm	%	66	N/A	58	57	64

[0084] The results set forth in the preceding tables demonstrate that the formulations containing surface modified filler have higher filler loading and thermal conductivity, while maintaining low modulus and film processibility relative to formulations prepared without such fillers.

[0085] Various modifications of the present invention, in addition to those shown and described herein, will be apparent to those skilled in the art of the above description. Such modifications are also intended to fall within the scope of the appended claims.

[0086] The foregoing description is illustrative of particular embodiments of the invention, but is not meant to be a limitation upon the practice thereof. The following claims, including all equivalents thereof, are intended to define the scope of the invention.

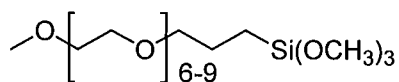
That which is claimed is:

1. A thermally-conductive interface material formulation comprising:
a thermosetting resin, and
a surface modified filler that is a reaction product of a covalently linked moiety of
a filler, and
a long chain molecule selected from the group consisting of

$$Y-(CH_2CH_2O)_m-(CH_2)_q-X$$
, wherein m is 1 or greater and q is 1 or greater,

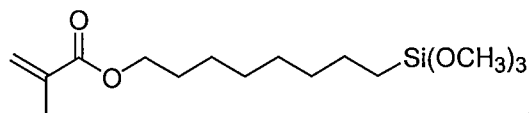
$$Y-(CH_2)_n-X$$
, wherein n is 2 or greater, and

$$Y-(CF_2)_p(CH_2)_z-X$$
, wherein p is 1 or greater and z is 1 or greater,
 wherein X is a functional group that covalently reacts with the filler, and
 wherein Y is an end group.
2. The formulation of claim 1 wherein X is selected from the group consisting of following:
trialkoxysilane, such as trimethoxysilane and triethoxysilane, isocyanate, carboxylic acid,
anhydride, maleate, fumarate, sulfonic acid, acyl chloride, and epoxide.
3. The formulation of claim 1 wherein Y is an end group selected from the group consisting
of an acrylate, methacrylate, anhydride, NH_2 , aromatic amine, epoxy, styrene, maleate, fumarate,
vinyl ether, oxetane, benzoxazine, cyanate ester, maleimide, vinyl ester, phenol, mercaptan,
isocyanate, an alkyl, an alkoxide, and a fluorinated alkyl.
4. The formulation of any of 1-3, wherein the long chain molecule is $Y-(CH_2CH_2O)_m-$
 $(CH_2)_q-X$, wherein X is a silane, and m is between 6 and 9.
5. The formulation of claim 4, wherein the long chain molecule is:



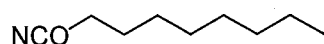
6. The formulation of any of claims 1-3, wherein the long chain molecule is $Y-(CH_2)_n-X$, X
is a silane, and n is 8 or greater.

7. The formulation of claim 6, wherein the long chain molecule is:



8. The formulation of any of claims 1-3, wherein the long chain molecule is $Y-(CH_2)_n-X$, wherein X is a isocyanate end group, and n is 8 or greater.

9. The formulation of claim 8, wherein the long chain molecule is:



10. The formulation of any of claims 1-9, wherein the filler is a an inorganic filler selected from the group consisting of aluminum oxide, aluminum nitride, boron nitride, magnesium oxide, zinc oxide, silicon carbide, silicon dioxide, beryllium oxide, antimony oxide, and mixtures thereof.

11. The formulation of any of claims 1-9, wherein the filler is aluminum oxide.

12. The formulation of any of claims 1-9, wherein the filler is selected from the group consisting of carbon nanotubes, graphene, fullerene, and graphite.

13. The formulation of any of claims 1-9, wherein the filler is aluminum oxide and comprises at least 75 wt.% of the formulation, and upon cure the formulation exhibits a melt viscosity less than 35,000 P and a storage modulus less than 15 GPa.

14. The formulation of any of claims 1-9, wherein the filler is aluminum oxide and comprises at least 80 wt.% of the formulation, and upon cure the formulation exhibits an a bulk thermal conductivity upon cure greater than 1.4 W/mK.

15. The formulation of claim 14, wherein upon cure the filler imparts a melt viscosity less than 30,000 P, and a storage modulus less than 15 GPa.

16. A B-staged aliquot of the formulation of any of claims 1-15.
17. A cured aliquot of the formulation of any of claims 1-15.
18. A curable film comprising a B-staged layer of the formulation of any of claims 1-15 on a suitable substrate thereof.
19. An assembly comprising a first article permanently adhered to a second article by a cured aliquot of a formulation according to claim 17.
20. A method for adhesively attaching a first article to a second article, said method comprising:
 - (a) applying an aliquot of the formulation of any of claims 1-15 to said first article,
 - (b) bringing said first and second articles into intimate contact to form an assembly wherein the space between said first article and said second article is substantially completely filled by the formulation applied in step (a), and thereafter
 - (c) optionally subjecting said assembly to conditions suitable to cure said formulation.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/035722

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 10-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/035722

A. CLASSIFICATION OF SUBJECT MATTER <i>C09K 5/08 (2006.01)</i> <i>C09K 5/14 (2006.01)</i> <i>C08K 3/00 (2006.01)</i> <i>C08K 9/04 (2006.01)</i> <i>C08K 9/06 (2006.01)</i> <i>H01L 21/00 (2006.01)</i>		
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) C09K 5/08, 5/14, C08K 9/04, 9/06, 3/00, H01L 21/00		
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) PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/0208429 A1 (YIMIN ZHANG et al) 19.08.2010	1-9, 16-20
A	WO 2011/059942 A2 (HENKEL CORPORATION) 19.05.2011	1-9, 16-20
A	US 2006/0275608 A1 (GENERAL ELECTRIC COMPANY) 07.12.2006	1-9, 16-20
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
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09 August 2016 (09.08.2016)		15 September 2016 (15.09.2016)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer E. Gavrikova Telephone No. (495) 531-64-81